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LXXIX.—THE REACTIONS OF SODIC ALCOHOLATES WITH TRIBROMTRINITROBENZOL.[1]

Second Paper.

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In our first paper on this subject we described some experiments which led to the replacement of nitro groups in symmetrical tribromtrinitrobenzol by ethoxy or methoxy radicles. These observations seemed to us of special interest because the three nitro groups are in the meta position in this compound, and, so far as we were aware, no case was known in which a nitro group in this position to others had been removed from the benzol ring. In fact the so-called rule of Laubenheimer stated that a nitro group is replaced only when it is in the ortho position to another. Even with the halogens, cases where a radicle in the meta position exercises a loosening effect on another are very rare, the only one which occurs to us being the conversion of symmetrical tribrombenzol into dibromanisol by the action of sodic methylate.[2]

Soon after the appearance of our paper C. A. Lobry de Bruyn published an account[3] of some experiments with symmetrical trinitrobenzol and sodic methylate from which he obtained dinitro-

[1] Presented to the American Academy. The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

[2] Blau: Monatsh. Chem. **7**, 630.

[3] Recueil trav. chim. **9**, 208.

anisol, thus again removing a nitro group in the meta position to others. At the same time, in an interesting discussion[1] of the replacement of nitro groups in aromatic compounds, he showed that Laubenheimer's rule must be abandoned, since para as well as ortho nitro compounds are attacked by alcoholates and other reageants with the removal of nitro groups. This publication brought to our notice an earlier paper[2] by him, in which he states that by the action of alcoholic potassic cyanide on metadinitrobenzol one nitro group is replaced by the ethoxy (or methoxy) radicle, but at the same time an atom of cyanogen is substituted for one atom of hydrogen, giving as the product $C_6H_3.NO_2.OC_2H_5.CN$. This curious result seems to have more affinity with the additions of hydrocyanic acid to nitrohalogen benzols studied by v. Richter[3] than to simple substitution; but nevertheless we have here the replacement of a meta nitro group by another radicle. As Lobry de Bruyn's later work was published almost simultaneously with ours (although a little later), and had grown out of his earlier researches, we felt that the study of substitutions of nitro groups in simple trinitro compounds should properly belong to him, and after a pleasant correspondence on the subject it has been agreed that he should follow out this line of work, while we confine ourselves, so far as the removal of nitro groups is concerned, to the completion of our study of tribromtrinitrobenzol.

At present, therefore, we know only three meta nitro compounds from which nitro groups have been removed: dinitrobenzol, symmetrical trinitrobenzol, and symmetrical tribromtrinitrobenzol.

Lobry de Bruyn's work shows that the removal of nitro groups observed by us is caused by the position of these nitro groups, but the presence of the three meta bromine atoms evidently also has a loosening effect on the nitro groups, as we have replaced two of these groups by ethoxy radicles, whereas in the trinitrobenzol only one was replaced.

In taking up the study of the subject again, we first examined the action of tribromtrinitrobenzol and sodic ethylate more carefully, to see whether the bromine atoms were not also affected by it, and found that in addition to the tribromnitroresorcin diethyl ether there is always formed a quantity of trinitrophloroglucin triethyl ether, $C_6(OC_2H_5)_3(NO_2)_3$, melting at 119°–120°; as, how-

[1] Recueil trav. chim. **9**, 210.
[2] *Ibid.* **2**, 205.
[3] Ber. d. chem. Ges. **4**, 465; **7**, 1145; **8**, 1418.

ever, this substance is easily decomposed by sodic hydrate, the amount of it obtained as such is small, unless special precautions are taken to exclude atmospheric moisture. When such precautions are not taken, the trinitrophloroglucin triethyl ether is converted into the diethyl ether $C_6OH(OC_2H_5)_2(NO_2)_3$, melting at 89°, or trinitrophloroglucin itself, $C_6(OH)_3(NO_2)_3$ (which melts at 167° instead of 158°, the point given by Benedikt,[1]), and these substances pass into the aqueous wash-waters as sodium salts. It follows therefore that the action of sodic ethylate on tribromtrinitrobenzol consists of the two following reactions, which take place parallel to each other:

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr.$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_2NO_2(OC_2H_5)_2 + 2NaNO_2.$$

We observed further, that, if benzol and alcohol were used as the solvents instead of alcohol alone, more of the phloroglucin ether was obtained than when the solvent was only alcohol, and this led us to study the action quantitatively by determining the amounts of sodic nitrite and bromide formed, when we found that the amount of nitrite averaged with the benzol and alcohol 33.49 per cent.; with alcohol alone, 45.92 per cent. There was also a difference in the reverse direction with the sodic bromide, but the percentages of this obtained under parallel conditions varied so materially that no careful comparison was possible. The percentages of sodic nitrite removed were, on the other hand, remarkably constant. We have not succeeded in finding any satisfactory explanation for this effect of the presence of benzol in promoting the formation of the trinitrophloroglucin triethyl ether (produced by the first reaction), and diminishing the amount of tribromnitroresorcin diethyl ether formed by the second reaction given above.

We have also tried the action of several other alcoholates on tribromtrinitrobenzol, obtaining the following compounds: $C_6Br_3NO_2(OCH_3)_2$, melting at 126°; $C_6(OCH_3)_3OH(NO_2)_2$, melting at 77–78°; $C_6(OC_3H_7)_3(NO_2)_3$, from normal propyl alcohol, melting-point 109°–110°; the corresponding iso-compound melting at 130°; and $C_6(OCH_2C_6H_5)_3(NO_2)_3$, melting at 171°. A quantitative comparison of the amounts of sodic nitrite formed by different alcoholates indicated that the percentage removed dimin-

[1] Ber. d. chem. Ges. **11**, 1376.

ishes as the molecular weight of the alcohol increases, but there were several exceptions to this general rule.

We have also found that sodic ethylate decomposes the triphenyl ether of trinitrophloroglucin, converting it into the triethyl ether, while phenol is set free; and that sodic ethylate when heated with the tribromnitroresorcin diethyl ether removes from it two atoms of bromine which are replaced by hydrogen, so that the product is bromnitroresorcin diethyl ether, $C_6H_2BrNO_2(OC_2H_5)_2$, melting at 115°;—an observation which will be of value in discovering the cause of the strange replacements of bromine by hydrogen so often found in the course of this work.

Part I.—Action of Sodic Ethylate on Tribromtrinitrobenzol.

In our earlier paper[1] on this subject we showed that sodic ethylate brought about a replacement of two of the nitro groups in tribromtrinitrobenzol by two ethoxy radicles forming tribromnitroresorcin diethyl ether, $C_6Br_2NO_2(OC_2H_5)_2$, as the principal product if alcohol was used as the only solvent and the mixture carefully cooled. There remained, however, several points which needed more careful examination, especially the effect upon the reaction of differences of temperature, the effect of using different solvents, and the source of the sodic bromide which was always formed in addition to the sodic nitrite. The results of our work on these subjects are given in the following paragraphs.

The experiments described in our first paper had led us to think that the tribromnitroresorcin diethyl ether was formed only when the mixture of tribromtrinitrobenzol and sodic ethylate was carefully cooled. To test the accuracy of this conclusion, we dissolved some tribromtrinitrobenzol in alcohol and a little benzol with the aid of heat, and added to the boiling solution, in small quantities at a time, enough sodic ethylate to give three molecules of the ethylate to each molecule of tribromtrinitrobenzol. As soon as all the ethylate had been added, the bright scarlet solution was allowed to cool, and then evaporated spontaneously. The aqueous washings of the residue gave a strong test for a nitrite, and also for a bromide. The portion insoluble in water was purified by crystallization from alcohol until it showed a melting-point of 100°

[1] This Journal **13**, 184.

(the tribromnitroresorcin diethyl ether melts at 101°), when it was analyzed with the following result:

0.2076 gram substance gave by Carius' method 0.2601 gram AgBr.

	Calculated for $C_4Br_2NO_3(OC_2H_5)_2$.	Found.
Bromine	53.57	53.32

This analysis, with the melting-point, leaves no doubt that the substance is the expected tribromnitroresorcin diethyl ether, and therefore that the temperature of the reaction does not affect the nature of the principal product. We have accordingly omitted the cooling in our subsequent preparations of this body, simply allowing the mixture of tribromtrinitrobenzol, sodic ethylate, and alcohol to stand over night at ordinary temperatures.

The Modification of the Action when Benzol is used as one of the Solvents.

To study this subject the following experiment was tried: 10 grams of tribromtrinitrobenzol were dissolved in dry benzol and an alcoholic solution of the sodic ethylate from 1.5 grams of sodium added (these proportions are essentially three atoms of sodium to each molecule of tribromtrinitrobenzol). The first drop of the solution of sodic ethylate turned red as it was added, the color fading to yellow as the drop mixed with the liquid, so that, after all the ethylate had been added, the liquid had assumed an orange-red color. No evolution of heat was observed during the reaction. To make sure that the action was complete, the mixture was allowed to stand over night in a corked flask at ordinary temperatures, and was then allowed to evaporate spontaneously, after which the residue was washed with water to remove the soluble salts.

Substances insoluble in Water.—The residue after washing with water was crystallized repeatedly from alcohol, and in this way a considerable quantity of the tribromnitroresorcin diethyl ether melting at 101° was obtained from the first crystals, while the mother-liquors yielded a smaller quantity of another substance which when pure melted at 119°–120°. This was dried at 100°, and analyzed with the following results:

I. 0.2159 gram substance gave 0.3284 gram CO_2 and 0.0914 gram H_2O.

II. 0.2080 gram substance gave 22 5 cc. N at 21° and 759.3 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found. I.	II.
Carbon	41.75	41.49	...
Hydrogen	4.35	4.70	...
Nitrogen	12.17	...	12.30

It contained no bromine. There can be no doubt, therefore, that the product was the triethyl ether of trinitrophloroglucin, and that the formation of this substance produced the sodic bromide which was always obtained by the action of sodic ethylate on tribromtrinitrobenzol.

Properties of Trinitrophloroglucin Triethyl Ether.—This substance crystallizes in long slender plates, terminated usually by one plane at a very sharp angle to the sides. These crystals are often united longitudinally into broader plates, which frequently have serrated ends, and may reach more than a centimeter in length and a millimeter in breadth. The color is white, but it turns brownish on exposure to the air. It melts at 119°–120°; is soluble in cold ethyl or methyl alcohol, freely soluble in either of these solvents when hot; very freely soluble in benzol, chloroform, or acetone; freely soluble in glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroïn; essentially insoluble in water, whether cold or hot. The three strong acids have no perceptible action on it, hot or cold, except that it is dissolved by hot strong nitric acid, but on dilution it is precipitated unchanged, to judge by the melting-point. We have tried no experiments on its saponification by the long-continued action of acids. A cold aqueous solution of sodic hydrate had no action upon it, and only a slight action when heated, but in alcoholic solution sodic hydrate decomposes it even in the cold, more rapidly when hot, forming a reddish-yellow solution of the sodium salt of a phenol.

In addition to the tribromnitroresorcin diethyl ether and trinitrophloroglucin triethyl ether, we have always obtained from the crystallization a considerable amount of a substance which accumulated in the mother-liquors and separated from its alcoholic solution as an oil solidifying after standing for some weeks. We have devoted a great deal of time to the study of this substance, because it appeared in such quantity that we thought it must be a principal product of our reaction; but this work has shown that it consists principally of the products already described, mixed with very little of an oily substance which prevents them from crystallizing as usual. In a preparation from 30 grams of tribrom-

trinitrobenzol, the mother-liquors gave 4.3 grams of the more-or-less liquid fraction, but this amount was reduced to 1.2 grams after removing the trinitrophloroglucin triethyl ether completely by treatment with alcoholic sodic hydrate, and the tribromnitroresorcin diethyl ether as nearly as possible by crystallization from alcohol of the mixture solidified by standing for several months. All our attempts to free the oily product completely from the tribromnitroresorcin diethyl ether have failed, so that we are unable to give any account of its composition.

Products soluble in Water.—In purifying the products of the action of sodic ethylate upon tribromtrinitrobenzol, the aqueous solution formed by washing the residue from spontaneous evaporation contained a large amount of organic matter, as was indicated by its orange-red color. In order to determine its nature, the solution was acidified with dilute sulphuric acid, which gave a precipitate, but did not remove all the organic matter present, since the filtrate still showed a strong yellow color. This precipitate was washed with water, in which it is nearly insoluble, until the washings ceased to show a yellow color, and then purified by converting it into its sodium salt, filtering the solution, reprecipitating with dilute sulphuric acid, and finally crystallizing from dilute alcohol until it showed the constant melting-point 89°, when it was dried *in vacuo* and analyzed with the following results:

0.2285 gram substance gave 0.3145 gram CO_2 and 0.0817 gram H_2O.

	Calculated for $C_6(OC_2H_5)_2OH(NO_2)_2$.	Found.
Carbon	37.85	37.53
Hydrogen	3.47	3.97

To confirm these results, a portion of the substance was treated with an aqueous solution of less than the calculated amount of sodic hydrate necessary to convert it into the sodium salt; the solution of the salt was filtered from the unaltered phenol, the filtrate evaporated to dryness, and the residue washed with benzol to remove any traces of the free phenol which might have dissolved in the water. It was then dried at 100°, and the sodium salt thus obtained analyzed with the following results:

I. 0.1498 gram substance yielded 0 0329 gram Na_2SO_4.

II. 0.2410 gram salt gave 0.0524 gram Na_2SO_4.

	Calculated for $C_4(OC_2H_5)_2ONa(NO_2)_2$.	Found. I.	II.
Sodium	6.78	7.11	7.04

These analyses leave no doubt that the substance is the diethyl ether of trinitrophloroglucin. As it has not been described heretofore, we add its properties.

Properties of the Diethyl Ether of Trinitrophloroglucin.—This substance crystallizes in square-ended, rather short prisms, or in longer flat needles, also, usually, with square ends, although sometimes instead of this they are very sharp; both forms are frequently arranged in fan-like groups. It has a straw-yellow color, and melts at 89°. Very freely soluble in ethyl or methyl alcohol, ether, benzol, glacial acetic acid, chloroform, or acetone; soluble in carbonic disulphide; very slightly soluble in ligroïn; slightly soluble in cold water, more soluble in hot; dilute alcohol is the best solvent for it. The three strong acids have no apparent action on it, hot or cold. Sodic hydrate dissolves it, forming an orange-red sodium salt, which crystallizes in fine needles. Ammonic hydrate dissolves it rather slowly, forming a yellow solution. Solutions of sodic or acid sodic carbonate also dissolve it with evolution of carbonic dioxide, forming yellow solutions; it is evident, therefore, that the substance possesses strongly acid properties.

The filtrate from the diethyl ether of trinitrophloroglucin, which had changed from red to yellow on acidification, after concentration on the water-bath deposited upon cooling rather ragged, thick yellow needles; but if the evaporation was carried on spontaneously, yellow hexagonal prisms were obtained, which dissolved in alkalies more easily than in water, and gave, according to the amount of alkali used, red or yellow salts, crystallizing in hair-like needles—properties which indicated that the substance was a polyatomic nitrophenol, probably the trinitrophloroglucin. This substance has been described by Benedikt[1] as crystallizing from water in hexagonal prisms, and melting at 158°; we accordingly purified our substance by crystallization from water, but found that it melted as high as 167°. In spite of the want of agreement between this melting-point and that given by Benedikt, the crystalline form and other properties indicated that the substance was trinitrophloroglucin, and this was proved to be the case

[1] Ber. d. chem. Ges. **11**, 1376.

by the following analyses. As Benedikt found that trinitrophloroglucin contains one molecule of water of crystallization, we examined our substance for this:

I. 0.7721 gram air-dried substance heated to 105° lost 0.0477 gram.

	Calculated for $C_6(OH)_3(NO_2)_3H_2O$.	Found. I.
Water	6.45	6.18

The air-dried substance lost 0.0015 gram at 56°, and showed a tendency to sublime at 105°.

II. 0.2126 gram compound, dried at 105°, gave 0.2105 gram CO_2 and 0.0304 gram H_2O.

III. 0.2260 gram compound, dried at 105°, gave 31.2 cc. N at 17° and 775.8 mm.

	Calculated for $C_6(OH)_3(NO_2)_3$.	Found. II.	III.
Carbon	27.58	27.01[1]	...
Hydrogen	1.15	1.59	...
Nitrogen	16.09	...	16.37

It is evident from these analyses that the substance is *trinitrophloroglucin*, and therefore it becomes important to explain the very marked difference between the melting-points observed by Benedikt and by us. We are inclined to ascribe this to the water of crystallization, as the melting-point 167° was obtained with the substance dried at 105° and used for analysis, whereas with samples which had been only air-dried (or dried at 50°) we obtained melting-points as low as 160°–161°, that is, only 2° or 3° above the 158° obtained by Benedikt.

In order to determine whether the formation of the trinitrophloroglucin and its diethyl ether was due to a direct reaction, or to the secondary reaction on the trinitrophloroglucin triethyl ether of some sodic hydrate formed by the moisture of the air acting on the sodic ethylate, the following experiment was tried: Absolute alcohol made in the usual way with quicklime was treated with a small quantity of sodium, and then the unaltered alcohol distilled off from the sodic alcoholate in a perfectly dry apparatus, which communicated with the outer air only through a drying-tube; to the distillate in the flask which served as a

[1] The percentages of carbon and hydrogen are as near to those required by the formula as could be expected when the difficulty of making a combustion of this explosive substance is considered.

receiver, a quantity of bright sodium was added as quickly as possible, after which it was closed at once with a cork carrying a drying-tube. When the reaction was at an end, and the solution of sodic ethylate had cooled, 5 grams of dry tribromtrinitrobenzol were added, and the mixture allowed to stand over night closed with the cork carring the drying-tube. The solution, which had turned red, was acidified with dilute sulphuric acid and allowed to evaporate spontaneously, when after purification it yielded 2 grams of the triethyl ether of trinitrophloroglucin instead of 0.12 gram, the usual yield when no special precautions were taken to exclude atmospheric moisture. It is evident, therefore, that the trinitrophloroglucin triethyl ether is formed at first, and afterward saponified wholly or in part by sodic hydrate produced by the action of moisture on the sodic ethylate. That most of this sodic hydrate is formed during the spontaneous evaporation of the alkaline solution was shown by two experiments, in which the ethyl ether of trinitrophloroglucin was treated with a solution of sodic ethylate, with all the precautions described above, except that in one of these experiments the alkaline liquid was allowed to evaporate spontaneously, when all the triethyl ether was saponified, the whole product being soluble in water, whereas in the other, which was acidified before evaporating, 0.65 gram of unaltered triethyl ether was recovered, 0.7 gram having been the amount used.

Lobry de Bruyn[1] has encountered similar difficulties in studying the action of sodic ethylate upon the unsymmetrical trinitrobenzol (1, 2, 4), as in this case considerable quantities of dinitrophenol were obtained, whereas with sodic methylate the dinitroanisol was the only organic product.

Experiments with Acetic Ester as the Solvent.

After we had found that the presence of benzol diminished the tendency of sodic ethylate to replace nitro groups in the tribromtrinitrobenzol, we tried some experiments on the action of other solvents. The choice here, however, was limited, because there are so few liquids belonging to a different class from benzol which have any considerable solvent action on the tribromtrinitrobenzol; in fact, acetone and acetic ester were the only ones easily obtained which fulfilled this condition, and acetone had to be rejected, as

[1] Recueil trav. chim. **9**, 191.

it seemed to take part in the reaction, giving a dark brownish red solution, very different from the orange-red obtained in all other cases. This result was not unexpected after the work of Freer[1] (published only in the preliminary paper at the time we tried this experiment), and since we did this work we have seen the paper of Janovsky,[2] describing the colors which he obtained by the action of acetone and potassic hydrate on dinitro compounds of the aromatic series.

In our first experiment with acetic ester we used the commercial article without especially drying it. The action was carried on in the usual way, 5 grams of tribromtrinitrobenzol being used. The aqueous washings gave tests for nitrite and bromide, but the organic product was found to consist principally of the tribromdinitrophenetol melting at 147°, described in our previous paper.[3] For greater certainty it was analyzed, with the following results:

I. 0.2972 gram substance gave by Carius' method 0.3721 gram AgBr.

II. 0.2788 gram substance gave 0.3535 gram AgBr.

	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$.	Found. I.	II.
Bromine	53.46	53.27	53.96

This experiment called our attention to a subject which we had already studied without any very definite result, that is, the conditions under which the phenetol $C_6Br_3(NO_2)_2OC_2H_5$ is formed, rather than the tribromnitroresorcin diethyl ether, $C_6Br_2NO_2(OC_2H_5)_2$. Our previous work had led us to the conclusion that the presence of a trace of water is favorable to the formation of the phenetol, as on one occasion when benzol not dried over sodium was used this substance was obtained, and in the experiment described in our previous paper, which yielded a quantity of the phenetol, common benzol was also used, whereas in all the preparations made by us with absolute benzol and alcohol not a trace of the phenetol has been found. On the other hand, in a repetition of the experiment with common benzol, and in one in which undried benzol and common, instead of absolute, alcohol were used, only the resorcin ether $C_6Br_2NO_2(OC_2H_5)_2$ was isolated. To test this question still further, we repeated the experiment described at the beginning of this section, using carefully dried acetic ester instead of the com-

[1] This Journal **12**, 355; **13**, 308; Freer and Higley: **13**, 322.
[2] Ber. d. chem. Ges. **24**, 971.
[3] This Journal **13**, 187.

mercial article, and obtained decidedly less of the phenetol with a large proportion of the tribromnitroresorcin diethyl ether, thus confirming, although not absolutely proving, our previous inference that the presence of a trace of moisture is favorable to the formation of the phenetol.

Action when Alcohol is the only Solvent used.

This action has been already described in our first paper, but after we had found, as described in the preceding sections, that the action when benzol was present took place in the two parallel reactions,

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr, \text{ and}$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2,$$

it became of interest to determine whether the first of these reactions took place if alcohol was the only solvent, or whether the action consisted of the second alone, as we had supposed when we published our first paper. A very little work was sufficient to prove the presence of the trinitrophloroglucin triethyl ether, or the phenols formed by its saponification, among the products of the reaction when alcohol was the only solvent, thus showing that the action in the two cases is parallel, although the first reaction takes place to a much more limited extent when alcohol is the only solvent, than when a mixture of alcohol and benzol is used. Our attempts to determine the relative amounts of the products of each of these two reactions are described in a later section.

Preparation of Tribromnitroresorcin Diethyl Ether and Trinitrophloroglucin Triethyl Ether.

It follows from what has been said in the preceding sections, that the best way to prepare tribromnitroresorcin diethyl ether is to allow tribromtrinitrobenzol (10 parts) to stand in the cold for twelve hours with an alcoholic solution of sodic ethylate (from 1.5 parts of sodium), then, after the solvent has evaporated spontaneously, to wash the residue with water, and after one crystallization of the insoluble part from alcohol, treat it in the cold with an alcoholic solution of sodic hydrate for about twelve hours to saponify the trinitrophloroglucin triethyl ether also present. The sodium salt thus formed is washed out, and the residue crystallized from alcohol until it shows the melting-point of 101°.

If, on the other hand, trinitrophloroglucin triethyl ether is to be prepared, the tribromtrinitrobenzol should be dissolved in anhydrous benzol (dried with sodium) and the alcoholic solution of sodic ethylate added to this solution. Every precaution should be taken to exclude even traces of moisture, and after the twelve hours standing the solution should be acidified with dilute sulphuric acid before allowing it to evaporate spontaneously. The residue, after washing with water, is purified by crystallization from alcohol, which separates the two ethers formed by the parallel reactions.

Quantitative Study of the Action of Sodic Ethylate on Tribromtrinitrobenzol.

After we had proved that this action takes place in these two different ways,

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr, \text{ and}$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_2NO_2(OC_2H_5)_2 + 2NaNO_2,$$

it became of interest to determine the relative extent of each of the parallel reactions under varying conditions, and the easiest way to do this was obviously to find the amount of sodic bromide and sodic nitrite formed, as the first must have proceeded from the reaction giving the trinitrophloroglucin triethyl ether, the second from that producing the tribromnitroresorcin diethyl ether. In addition to this we have weighed the amount of organic matter formed, and have made some not very successful attempts to determine the amount of its several constituents. The method adopted was the following: A weighed quantity of tribromtrinitrobenzol mixed with the solvent and the ethylate in the proportion of three atoms of sodium to each molecule, stood over night in a corked flask. The liquid was then allowed to evaporate spontaneously, and the residue washed thoroughly with water. The weight of the organic matter insoluble in water was taken, and also that of the aqueous solution which contained all the sodium salts; this was then divided into weighed parts, one of which was acidified with nitric acid, and after filtering out and weighing the diethyl ether of trinitrophloroglucin the amount of sodic bromide it contained was determined with argentic nitrate. The second portion of the aqueous liquid was used for the determination of the amount of sodic nitrite, but it was not easy to find a method which would

be applicable in this case. The common way of determining a nitrite with potassic permanganate was inadmissible, because of the presence of organic matter. The urea-method in its usual form was also inapplicable because of the presence of sodic carbonate, but finally by modifying it in the following way we succeeded in obtaining satisfactory results: The weighed portion of the solution to be tested, mixed with a sufficient quantity of urea, was poured into a little flask, and a small test-tube containing dilute sulphuric acid put into the flask supported in a vertical position by a piece of platinum wire projecting from its upper end and resting against the neck of the flask. The apparatus was then filled with carbonic dioxide from a heated tube containing magnesite, after which by shaking the flask the sulphuric acid was added to its contents in small quantities at a time, and the nitrogen given off collected over a solution of potassic hydrate, and measured in the usual way. It is necessary to heat the flask gently toward the end of the operation to drive off all the nitrogen. One-half of the nitrogen collected is derived from the sodic nitrite. To test the accuracy of the method two determinations of the nitrogen in commercial sodic nitrite were made by it, which gave,—

		Found.
Nitrogen	18.09	18.11

and as they agreed with each other, and came tolerably near to the usual percentage of nitrogen in commercial sodic nitrite (between 19 and 20 per cent.), it was evident that the method was accurate enough for our purposes. A third portion of the aqueous liquid was in two experiments used for the determination of the trinitrophloroglucin, but we give our results with a great deal of hesitation, as we were unable to find any satisfactory quantitative method; methods based upon extraction with an organic solvent, or the precipitation of the barium salt, which Benedikt says is insoluble, led to no result. We were therefore driven to determining the amount of nitrogen in the residue obtained by evaporating to dryness a portion of the aqueous solution acidified with sulphuric acid, and calculating from this the amount of trinitrophloroglucin, on the assumption, which at best can be but approximately correct, that this was the only substance containing nitrogen left in the residue.

Experiments in which Alcohol was the only Solvent used.—I. Weight taken, 10.556 grams. Weight of aqueous solution, 135.4

grams; 8.6 grams solution gave 16.9 cc. N from the $NaNO_2$ at 23° and 763.8 mm.; 28.2 grams solution gave 1.1718 grams AgBr; 20.8 grams solution gave, after the nitrous acid had been expelled by sulphuric acid, 8.2 cc. N at 23° and 767.8 mm.: 54.4 grams solution gave 0.808 gram diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 6.97 grams.

II. Weight taken, 10.1582 grams. Weight of aqueous solution, 164.55 grams; 15.95 grams solution gave 24.65 cc. N from $NaNO_2$ at 26.5° and 765 mm.; 58.45 grams solution gave 1.6583 grams AgBr, and yielded 0.8499 gram of the diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 5.78 grams.

III. Weight taken, 1.0366 grams. Weight of aqueous solution, 121.4 grams; 62.5 grams solution gave 13.6 cc. N from $NaNO_2$ at 21° and 765.2 mm.; 58.9 grams solution gave 0.2700 gram AgBr. Organic matter insoluble in water = 0.48 gram.

IV. Weight taken, 10 grams.[1] Weight of aqueous solution, 142.9 grams; 13.7 grams solution gave 25.7 cc. N from $NaNO_2$ at 29.5° and 759.2 mm.; 55.1 grams solution gave 1.9029 grams AgBr. 1.7 grams diethyl ether of trinitrophloroglucin were obtained from 10 grams used. Weight of organic matter insoluble in water = 6.4 grams.

V. Weight taken, 10 grams.[1] Weight of aqueous solution, 114.8 grams; 14.6 grams solution gave 32.3 cc. N from $NaNO_2$ at 28° and 764.1 mm.; 48.7 grams solution gave 0.9573 gram AgBr; 2.4 grams diethyl ether of trinitrophloroglucin were obtained from 10 grams used. Weight of organic matter insoluble in water = 5.6 grams.

The results of these experiments are given in tabular form at the end of the next section.

Experiments in which Benzol was the Principal Solvent used.— VI. Weight taken, 10.0220 grams. Weight of aqueous solution, 126.65 grams; 11.7 grams solution gave 17.15 cc. N from $NaNO_2$ at 24° and 764.5 mm.; 28.7 grams solution gave 1.6952 grams AgBr; 24.7 grams solution gave, after the nitrous acid had been expelled by sulphuric acid, 12.2 cc. N at 25° and 766.1 mm. Acid precipitated from these 24.7 grams solution 0.3374 gram diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 4.99 grams.

[1] This weight is accurate only to tenths of a gram.

VII. Weight taken, 10.1976 grams. Weight of aqueous solution, 135.2 grams; 19.3 grams solution gave 27.2 cc. N from $NaNO_2$ at 25° and 750.9 mm.; 43.9 grams solution gave 1.6158 grams AgBr; 72 grams solution gave 1.4724 grams diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 5.51 grams.

VIII. Weight taken, 1.2524 grams. Weight of aqueous solution, 37.3 grams; 24.2 grams solution gave 14.3 cc. N from $NaNO_2$ at 19° and 771.5 mm.; 13.1 grams solution gave 0.4097 gram AgBr. Organic matter insoluble in water = 0.55 gram.

IX. Weight taken, 1.2682 grams. Weight of aqueous solution, 38.1 grams; 19.7 grams solution gave 12 cc. N from $NaNO_2$ at 24° and 767.3 mm.; 18.4 grams solution gave 0.5082 gram AgBr. Organic matter insoluble in water = 0.58 gram.

X. Weight taken, 1.2287 grams. Weight of aqueous solution, 53 65 grams; 17.65 grams solution gave 7.7 cc. N from $NaNO_2$ at 25° and 766.1 mm.; 18.9 grams solution gave 0.2664 gram AgBr and 0.0854 gram diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 0.68 gram.

In the following tables the first column gives the number of the experiment, and the weight of tribromtrinitrobenzol used; the second, the percentage of nitrogen removed as sodic nitrite referred to the total amount of nitrogen which could be removed from the tribromtrinitrobenzol by this reaction, that is, two out of the three atoms of nitrogen, because the product $C_6Br_3NO_2(OC_2H_5)_2$ contains one nitro group; the third column gives the percentage of the total bromine removed as sodic bromide; the fourth, the weight of the organic matter insoluble in water; the fifth, the weight of the diethyl ether of trinitrophloroglucin; and the sixth, the weight of trinitrophloroglucin calculated from the volume of nitrogen obtained from the residue after acidification with sulphuric acid.

TABLE I.—*Action of Sodic Ethylate in Ethyl Alcohol.*

	Weight of $C_6Br_3(NO_2)_3$ used.	Percentage of Nitrogen.	Percentage of Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH(NO_2)_3$.	Weight of $C_6(OH)_3(NO_2)_3$.
I.	10.556	45.88	42.53	6.97	2.0	0.38
II.	10.1582	44.85	36.67	5.78	2.39	...
III.	1.0366	46.95	42.85	0.48	...	...
IV.	10.	46.86	39.39	6.4	1.7	...
V.	10.	45.06	18.02	5.6	2.4	...

TABLE II.—*Action of Sodic Ethylate with Benzol and Alcohol.*

	Weight of $C_6Br_3(NO_2)_3$.	Nitrogen.	Bromine.	Weight of Organic Matter.	Weight of $C_6(OC_2H_5)_2OH(NO_2)_3$.	Weight of $C_6(OH)_3(NO_2)_3$.
VI.	10.022	33.58	59.54	4.99	1.73	0.44
VII.	10.1976	33.09	38.91	5.51	2.8	...
VIII.	1.2524	33.03	74.32	0.55	...	...
IX.	1.2682	33.31	66.21	0.58	...	...
X.	1.2287	34.42	49.10	0.68	...	...

An examination of these tables shows that the percentages of nitrogen removed are fairly constant under each set of conditions, the maximum differences being, in Table I, 2.1 per cent., in Table II, 1.39 per cent.,—which are surprisingly small when the nature of the process and the roughness of the manipulations are considered. These numbers, therefore, are well fitted to give an idea of the effect on the reactions of the presence of benzol, and they show that it diminishes the amount of sodic nitrite formed, since the percentage of nitrogen removed when alcohol alone is present, averages 45.92 (maximum 46.95, minimum 44.85), whereas if the solvent is partly benzol the average percentage falls to 33.49 (maximum 34.42, minimum 33.03).

On the other hand, no agreement is found in the amounts of bromine removed as sodic bromide, the maximum difference in Table I being 24.83 per cent., in Table II 35.41 per cent.; but in spite of this these results show that the presence of benzol favors the removal of bromine, since of the five determinations of bromine in presence of benzol (Table II), only one (38.91 per cent.) is below the largest percentage of bromine obtained (42.85 per cent.) when alcohol was the only solvent (Table I), and most of those in Table II are very far above those in Table I.

As to the numerical relations between the percentages of inorganic compounds formed under the two sets of conditions, it is to be observed that in the alcohol series the amounts of nitrite and bromide are approximately equal. In the benzol series the amount of nitrite is almost exactly one-third of the total amount which could have been formed, and is in some cases about one-half that of the bromide. In most cases, between 80 and 90 per cent. of the tribromtrinitrobenzol used is accounted for by the amounts of inorganic salts formed. The experimental work is not accurate enough to allow a more careful discussion of this part of the sub-

ject, as not enough attention was paid to various details, such, for instance, as maintaining a constant temperature, and measuring accurately the amounts of solvent used.

In all the experiments with benzol given in Table II free alcohol was also present. To determine what influence this had on the reaction, we made another experiment, in which all free alcohol was carefully excluded, so that in this case benzol was the only liquid present.

XI. Weight taken, 5.0453 grams. Weight of aqueous solution, 83.4 grams; 19.6 grams solution gave 23.8 cc. N at 28.5° and 760.1 mm.; 43.4 grams solution gave 1.9610 grams AgBr and 1.55 grams of the diethyl ether of trinitrophloroglucin. Organic matter insoluble in water = 2.75 grams.

From these results 35.34 per cent. of nitrogen and 59.62 per cent. of bromine are obtained. The percentage of nitrogen, when benzol and alcohol were used as the solvents, averaged 33 49, so that this experiment shows that the presence of alcohol does not materially affect the result. The somewhat high percentage of nitrogen in this experiment may be due to the fact that the mixture stood two days instead of the usual twelve hours. This subject of the effect of time on the action will be discussed later in the paper.

We have also made two quantitative determinations, in which acetic ester was used with a little alcohol as the solvent.

XII. Weight taken, 1.0412 grams. Weight of aqueous solution, 58 grams; 17.5 grams solution gave 0.63 cc. N at 23.5° and 758.9 mm.; 40.5 grams solution gave 0.4504 gram AgBr.

XIII. Weight taken, 1.0271 grams. Weight of aqueous solution, 49.1 grams; 18 grams solution gave 2.8 cc. N at 22.5° and 760.8 mm.; 31.1 grams solution gave 0.4902 gram AgBr.

		Nitrogen.	Bromine.
XII.	1.0412	3.62	50.06
XIII.	1.0271	13.49	60.15

We are inclined to regard No. XII with suspicion; but No. XIII alone shows that acetic ester has an even more unfavorable influence than benzol on the formation of the sodic nitrite; this is probably due to the fact that in this case there is a tendency to form the tribromdinitrophenetol, which would yield half as much sodic nitrite as the tribrommononitroresorcin diethyl ether formed when benzol was used.

Relative Yields of the Organic Products.—After we had determined the amounts of sodic bromide and nitrite formed by the two parallel reactions,

$$C_6Br_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaBr, \text{ and}$$
$$C_6Br_3(NO_2)_3 + 2NaOC_2H_5 = C_6Br_3NO_2(OC_2H_5)_2 + 2NaNO_2,$$

we tried to get an idea of the relative yields of the organic products. This could be done with some approach to accuracy in the case of the reaction which produces sodic bromide, because during the work most of the trinitrophloroglucin triethyl ether was converted into the salts of trinitrophloroglucin or its diethyl ether, both of which can be easily separated from the other organic products on account of their solubility in water. With the tribromnitroresorcin diethyl ether, on the other hand, no such approach to accuracy was obtained, because it could be purified only by crystallization, and a large portion of it remained mixed with the viscous impurity already mentioned. To obtain the following results, the organic matter insoluble in water, obtained from two experiments, was repeatedly crystallized from alcohol, until as much pure tribromnitroresorcin diethyl ether and trinitrophloroglucin triethyl ether had been obtained as possible. To the amount of the latter, which was very small, were added the calculated amounts of the triethyl ether corresponding to the quantities found of free trinitrophloroglucin and its diethyl ether. Two pairs of experiments were studied in this way, one from the series in which alcohol was the only solvent, and one from that in which benzol was used.

Experiments I and II.—Alcohol the only solvent. 20.71 grams tribromtrinitrobenzol gave 12.75 grams organic matter insoluble in water, from which were obtained 5.11 grams $C_6Br_3NO_2(OC_2H_5)_2$, 1.4 grams same slightly impure, 5.1 grams semi-liquid fraction from the mother-liquor, and 0.49 gram $C_6(OC_2H_5)_3(NO_2)_3$. From the aqueous solution 4.39 grams $C_6OH(OC_2H_5)_2(NO_2)_3$ were obtained, corresponding to 4.77 grams triethyl ether, and 0.78 gram[1] $C_6(OH)_3(NO_2)_3$, corresponding to 1.03 grams triethyl ether, making the total yield of triethyl ether 6.29 grams.

Experiments VI and VII.—Benzol present. 20.21 grams tribromtrinitrobenzol gave 10.50 grams organic matter insoluble in

[1] These numbers are only estimates, as the amounts of trinitrophloroglucin were determined only in Nos. I and VI, the weight found being doubled to give the numbers. It is to be remembered also that our method for determining the trinitrophloroglucin was far from satisfactory.

water, from which were obtained 3.25 grams $C_6Br_2NO_2(OC_2H_5)_2$, 1.36 grams $C_6(OC_2H_5)_2(NO_2)_2$, and somewhat less than 6 grams semi-liquid fraction from mother-liquors. From aqueous solution were obtained 4.53 grams $C_6OH(OC_2H_5)_2(NO_2)_2$, corresponding to 4.93 grams triethyl ether, and 0.88 gram[1] $C_6(OH)_2(NO_2)_2$, corresponding to 1.16 grams triethyl ether, making total yield triethyl ether 7.45 grams.

These results confirm the inference drawn from the percentage of sodic nitrite and bromide, that the presence of benzol is unfavorable to the reaction by which sodic nitrite is formed, but promotes that which yields sodic bromide; a fact which is shown more plainly by this collection of the results in tabular form:

	$C_6(OC_2H_5)_2(NO_2)_2$.	$C_6Br_2NO_2(OC_2H_5)_2$.
Alcohol alone (I and II)	6.29 grams.	5.11[1]
Benzol and alcohol (VI and VII)	7.45	3.25[1]

All our results, therefore, show that the presence of benzol is favorable to the elimination of bromine, unfavorable to that of nitro groups. The most probable theoretical explanation of this observation which has occurred to us depends on the effect of the change of solvents upon the amounts of the salts precipitated, but any discussion of this theory at present would not be worth while, because the principle on which it rests has not been tested by experiment, so far as we can find.

We have not succeeded in finding the cause of the very marked variations in the amounts of sodic bromide shown in Tables I and II. At first we feared they might be due to defects in our experimental work, but that this is not the case is shown by the following comparison of the weights of trinitrophloroglucin triethyl ether actually found with the amounts of this substance calculated from the percentages of bromine eliminated as sodic bromide in the same experiment. We have selected this body for the comparison because, as has been already stated, these weights were determined with a fair degree of accuracy.

	Calculated.	Found.
Alcohol alone (I and II)	6.30	6.29
Alcohol and benzol (VI and VII)	7.62	7.45

The agreement is much closer than we had any right to expect, and shows that the differences in the percentages of bromine are

[1] These numbers are only approximations to the true yields.

due to absolute variations in the extent of the reaction by which the bromine is removed, since experiments VI and VII differ in this respect very widely (VI 59.54 per cent. of bromine, VII 38.91 per cent. of bromine); and yet the amount of the trinitrophloroglucin triethyl ether calculated from these different percentages of bromine corresponds almost exactly to that obtained experimentally.

Part II.—Action of other Alcoholates on Tribromtrinitrobenzol.

In addition to the work with sodic ethylate just described, we have tried the action of the sodium compounds of other alcohols on the tribromtrinitrobenzol, and give in the first place descriptions of the new compounds thus obtained, followed by a series of quantitative experiments similar to those tried with the ethylate.

Sodic Methylate.

The organic compound insoluble in water obtained by the action of sodic methylate on tribromtrinitrobenzol consisted in every experiment we have tried of the tribromnitroresorcin dimethyl ether, melting at 126°, and already described in our first paper;[1] as, however, we found that a considerable amount of sodic bromide was formed in these experiments, we turned our attention to the aqueous washings of this organic matter, in which it was evident that the product formed by the removal of the bromine was to be sought. Upon acidifying this aqueous solution with dilute sulphuric acid, a copious precipitate was obtained, which was only slightly soluble in water, and was purified by crystallization with the following precautions. The substance was dissolved in as small a quantity as possible of cold alcohol, water was then added until it began to grow turbid, when the solution was cleared by the addition of a drop or two of alcohol, and allowed to evaporate spontaneously, all these operations being carried on in the cold. When it showed the constant melting-point 77°–78°, it was dried and analyzed with the following results:

0.2298 gram substance gave 0.2792 gram CO_2 and 0.0597 gram H_2O.

	Calculated for $C_6(OCH_3)_2OH(NO_2)_2$.	Found.
Carbon	33.22	33.13
Hydrogen	2.42	2.89

[1] This Journal **13**, 188.

To confirm this result the sodium salt was made and analyzed; for this purpose 1 gram of the substance was treated with 0.1 gram of sodic hydrate dissolved in a little water, that is, decidedly less sodic hydrate than would be needed to convert the whole of the substance into its salt. The yellow solution thus obtained was evaporated to dryness at 100°, washed with benzol to remove the small quantity of the free phenol which had dissolved in the water, dried at 100°, and analyzed with the following result:

0.3730 gram salt gave 0.0874 gram Na_2SO_4.

	Calculated for $C_6(OCH_3)_2ONa(NO_2)_2$.	Found.
Sodium	7.39	7.59

These analyses and the analogy with the corresponding ethyl compound leave no doubt that the substance is the dimethyl ether of trinitrophloroglucin.

Properties of the Dimethyl Ether of Trinitrophloroglucin, $C_6(OCH_3)_2OH(NO_2)_3$.—The substance crystallizes with the precautions given above in long slender needles, with a slightly yellowish tinge, which melt at 77°–78°, and are very soluble in ethyl alcohol, methyl alcohol, ether, benzol, chloroform, acetone, or glacial acetic acid; soluble in carbonic disulphide; slightly soluble in ligroïn; somewhat soluble in cold water, more soluble in hot. With alkalies it forms reddish yellow salts. Strong sulphuric or hydrochloric acid does not act on it; it dissolves in strong nitric acid, but seems to be precipitated unchanged by dilution.

We also obtained a small amount of another substance with a higher melting-point, but not in sufficient quantity to characterize it.

Action of Sodic Propylate on Tribromtrinitrobenzol.

4 grams of normal propyl alcohol were mixed with anhydrous benzol, and treated with 1.5 grams of metallic sodium until all the sodium had disappeared; the reaction ran slowly, and was assisted by a gentle heat. The sodic propylate thus obtained was carefully cooled, and then a benzol-solution of 10 grams of tribromtrinitrobenzol added in small portions at a time, shaking and cooling with water after each addition. The proportions are about three atoms of sodium and three molecules of propyl alcohol to

each molecule of tribromtrinitrobenzol. As the first portions of the solutions were mixed the liquid turned blood-red, and this color, which at first faded to yellow on shaking, became permanent as more of the solution of tribromtrinitrobenzol was added. The mixture, which at no time showed a rise of temperature, was allowed to stand over night in a corked flask, and then the solution was filtered from a deposit of solid matter, which, after drying off the benzol, gave tests for a bromide and a nitrate. The benzol solution to which the solid not used for the above tests had been added was treated with water, and then acidified with dilute sulphuric acid, washed thoroughly, and, after most of the benzol had been recovered by distillation, the rest was distilled off in a current of steam. The residue thus obtained was oily, but solidified after standing for some time; it was then purified by crystallization from alcohol until it showed the constant melting-point 109°–110°, when it was dried at about 70°, and analyzed with the following results:

0.2366 gram substance gave 0.4058 gram CO_2 and 0.1214 gram H_2O.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.78
Hydrogen	5.43	5.70

The substance gives no test for bromine when heated on a copper wire. These results prove that it is the normal propyl ether of trinitrophloroglucin.

The aqueous solution, acidified with sulphuric acid, from which the benzol had been separated gave on extraction with ether a small amount of a yellow substance, which seemed to be trinitrophloroglucin, but was not present in sufficient amount for complete identification.

Properties of the Normal Tripropyl Ether of Trinitrophloroglucin, $C_6(OC_3H_7)_3(NO_2)_3$.—This substance crystallizes in plates often as much as 3 mm. long and 1 mm. broad, which under the microscope are seen to be made up of a number of flat prisms with square ends united by their longer sides, and usually much striated on lines parallel to both sets of edges. Its color is white with a very slight yellowish tinge, and it turns yellowish brown on standing exposed to the air. It melts at 109°–110°, and is soluble in cold ethyl or methyl alcohol, more freely when hot; freely

soluble in ether, benzol, chloroform, acetone, or carbonic disulphide; soluble in glacial acetic acid; slightly soluble in ligroïn, or in water whether hot or cold. Neither strong sulphuric, strong nitric, nor strong hydrochloric acid has any apparent action on it, whether cold or hot. The best solvent for it is boiling alcohol.

In another experiment no benzol was used, but the tribromtrinitrobenzol suspended in propyl alcohol was treated with sodic propylate. The product in this case was an oil which did not solidify even after standing for three months. We accordingly tried to purify it by treatment with a cold solution of sodic hydrate, and in this way obtained an orange solution, from which trinitrophloroglucin was easily isolated, pointing to the presence of the tripropyl ether of this body in the oil. After we could obtain no more of the sodium salt of the trinitrophloroglucin by further action of sodic hydrate, the oil was washed with water, dissolved in alcohol, precipitated again with water, and dried at 100°, when we hoped an analysis might throw some light on its composition; but in this we were disappointed, as a determination of the amount of bromine gave 45.29 per cent., whereas the tribromnitroresorcin dipropyl ether, which we hoped might have been formed, should contain 50.42 per cent. of bromine. As we could find no better way of purifying this substance, we have been forced to leave undecided the nature of the product formed by the replacement of nitro groups in tribromtrinitrobenzol by propoxy radicles. Fortunately, it is not a point of great importance.

Action of Sodic Isopropylate on Tribromtrinitrobenzol.

4 grams of isopropyl alcohol were converted into its sodium compound by treatment with 1.5 grams of sodium in anhydrous benzol, when it was found that the isopropyl alcohol acts on sodium more energetically than normal propyl alcohol, but both act less readily than ethyl alcohol. The isopropylate thus obtained was allowed to act on 10 grams of tribromtrinitrobenzol under the conditions described in the preceding section. The phenomena observed in this case were the same as those described for the normal propylate except that a slight rise of temperature from the reaction was observed. The solid deposited over night gave a strong test for sodic bromide and a distinct test for sodic nitrite.

The principal organic product was obtained and purified in the way given under the normal propyl compound until it showed the constant melting point 130°, when it was dried at 100°, and analyzed with the following results:

0.2280 gram substance gave 0.3876 gram CO_2 and 0.1182 gram H_2O.

	Calculated for $C_6(OC_3H_7)_3(NO_2)_3$.	Found.
Carbon	46.51	46.36
Hydrogen	5.43	5.76

The substance gave no test for bromine when heated with cupric oxide. A small amount of trinitrophloroglucin seemed to be formed as a secondary product in preparing the substance analyzed above.

Properties of the Triisopropyl Ether of Trinitrophloroglucin, $C_6(OC_3H_7)_3(NO_2)_3$.—This substance crystallizes in plates often 1 cm. long, made up of flattened prisms united by their longer sides. These prisms are terminated by two planes at an obtuse angle to each other, and seem to belong to the monoclinic system. It is white when first prepared, but gradually takes on an orange color on exposure to the air. It melts at 130°, and is not very soluble in cold ethyl or methyl alcohol, more soluble in hot; very soluble in benzol or chloroform; freely in ether or acetone; soluble in carbonic disulphide; slightly soluble in cold glacial acetic acid, freely when hot; very slightly soluble in ligroïn, and nearly insoluble in water whether cold or hot. The three strong acids have no apparent action on it whether cold or hot. The best solvent for it is boiling alcohol.

Action of Sodic Benzylate on Tribromtrinitrobenzol.

The sodic benzylate used was prepared as follows: To 1.3 grams of sodium mixed with anhydrous benzol and heated in a flask with a return-condenser, 6.5 grams of benzyl alcohol were added in small quantities at a time, and the heating continued until all the sodium had disappeared, which usually was not till after four hours. The benzyl alcohol therefore acts with sodium much more slowly than any of the other alcohols used by us. In this way we obtained a benzol solution of the sodic benzylate,[1]

[1] Since this part of our work was finished, Brühl and Biltz have published similar observations on other alcoholates in Ber. d. chem. Ges. **21**, 649 (1891).

which remained clear after it had cooled until it was shaken, when the solid separated in a gelatinous state. To the mixture of gelatinous sodic benzylate and benzol thus obtained a benzol-solution of 9 grams of tribromtrinitrobenzol was added; that is, for each molecule of tribromtrinitrobenzol we used three molecules of sodic benzylate.[1] The mixture was allowed to stand in the cold over night, the orange-red solution thus formed evaporated to dryness on a steam radiator at temperatures below 70°, and the residue washed with water and afterward with alcohol, after which it was purified by crystallization from a mixture of benzol and alcohol, until it showed the constant melting-point 171°. The analyses of the substance dried at 100° gave the following results:

I. 0.2038 gram substance gave 0.4546 gram CO_2 and 0.0752 gram H_2O.

II. 0.2678 gram substance gave 18.8 cc. N at 25° and 765.3 mm.

	Calculated for $C_6(OC_7H_7)_3(NO_2)_3$.	Found. I.	II.
Carbon	61.01	60.84	...
Hydrogen	3.96	4.10	...
Nitrogen	7.91	...	7.89

The substance gave no test for bromine when heated with cupric oxide.

10 grams of tribromtrinitrobenzol gave only 1.5 grams of the tribenzyl ether of trinitrophloroglucin, the analysis of which is given above, that is, less than 13 per cent. of the theoretical yield. This substance, therefore, is not by any means the principal product of the reaction. What the other products are will be discussed after the description of the properties of the benzyl ether.

Properties of the Trinitrophloroglucin Tribenzyl Ether.—This substance crystallizes from a mixture of alcohol and benzol in slender white needles forming a thick mat. It turns yellowish brown on exposure to the air, and melts at 171°; is slightly soluble even in hot alcohol, less soluble still in cold; somewhat more soluble in methyl than in ethyl alcohol; very freely soluble in benzol, chloroform or acetone; freely in carbonic disulphide; soluble in glacial acetic acid; very slightly soluble in ligroïn; essentially insoluble in water, whether cold or hot. The best solvent for it is a mixture

[1] The same principal product was obtained in a subsequent experiment with only two molecules of sodic benzylate. In most cases a slight excess of benzyl alcohol was used.

of alcohol and benzol. Strong sulphuric acid does not seem to act on it until charring sets in; strong nitric acid does not act on it in the cold, but seems to oxidize it when hot; strong hydrochloric acid has no apparent action on it, hot or cold.

Other Products of the Action of Sodic Benzylate on Tribromtrinitrobenzol.—To obtain these substances the aqueous and alcoholic washings mentioned above were evaporated to dryness, and the oily portion separated by extraction with a little alcohol from the salts. These, it was found, were a mixture of the sodium salt of trinitrophloroglucin with sodic bromide and nitrite, from which the trinitrophloroglucin was easily obtained, and identified by the melting-point 167°, and by analysis. It is one of the principal products of the reaction, and in fact most of the trinitrophloroglucin used for the analyses given in the first part of this paper was obtained in this way.

The oily material separated by the alcohol consisted mostly of the excess of benzyl alcohol, but on warming it we perceived the smell of benzyl bromide, and also suffered from its violent action on the eyes. Accordingly some of it, carefully washed to remove any sodic bromide, was boiled with an alcoholic solution of sodic sulphide, when it gave a strong smell of benzyl sulphide, and the water with which it was washed gave a faint test for bromine with chlorine-water. We did not succeed, however, in isolating the benzyl sulphide, which at best must have been present in very small quantity. Another similar oil, after thorough washing with water, was boiled with sodic acetate and alcohol, then water was added, which after being freed from the organic matter gave a slight test for bromine with chlorine-water. In another experiment the original product, after acidification with dilute sulphuric acid, was distilled with steam, and the oily distillate, having been thoroughly washed with water, was boiled with alcoholic sodic acetate, when it yielded a very strong test for a bromide with chlorine-water. These experiments have convinced us that in these three preparations a small quantity of benzyl bromide was present in the product of the reaction, although we have not succeeded in isolating the benzyl bromide itself, or one of its derivatives. This did not proceed from an impurity of benzyl bromide in the benzyl alcohol used, since after boiling it with an alcoholic solution of sodic acetate no test for sodic bromide could be obtained; it must have been formed, therefore, either in the course

of the reaction, or in the subsequent processes of purification. It is barely possible that this latter supposition may account for it in the last case, where the strongest test for bromine was obtained, as this was acidified before distillation with steam, and hydrobromic acid produced by the sulphuric acid and sodic bromide might have converted some of the excess of benzyl alcohol into benzyl bromide, although this seems highly improbable, because the solution was kept throughout in a very dilute state. In the two previous cases however, this explanation cannot apply, as no acid whatever had been added, so that no hydrobromic acid could have been formed; we are forced therefore to assume that the benzyl bromide was formed by the direct reaction and not by a secondary one, and under these circumstances the following reaction is the only one which seems to us admissible:

$$3C_7H_7ONa + C_6Br_3(NO_2)_3 = C_6(ONa)_3(NO_2)_3 + 3C_7H_7Br.$$

This is certainly very improbable, and we should add that, when we tried to confirm it by a repetition of the experiment, we did not succeed in detecting any benzyl bromide in the product. At first sight it would seem that a reaction the reverse of that given above would be more probable, but we proved that this was not the case by a special experiment, which showed that benzyl bromide had no action on the sodium salt of trinitrophloroglucin under the conditions used by us. We may add that amyl bromide also has no action under these conditions. On the other hand, there is little doubt that the benzyl bromide, if formed by this reaction, would act on the sodic benzylate forming benzyl ether. Accordingly, we tried to isolate benzyl ether from the oily product of the reaction by distilling off the excess of benzyl alcohol; there was so little of the residue which did not pass over at 207° that it was impossible to purify it properly; such as it was, however, it gave results on analysis agreeing with those calculated for benzyl alcohol (carbon, 76.70 instead of 77.78). We conclude, therefore, that if the reaction given above takes place, it is only to a very moderate extent, the principal reaction being the formation of the trinitrophloroglucin tribenzyl ether, which was then more or less saponified by the sodic hydrate formed by the action of atmospheric moisture on the sodic benzylate. We have not succeeded in detecting the organic substance formed by the removal of one or more nitro groups, as indicated by the appearance of sodic nitrite among the products.

Sodic Isobutylate or *Sodic Isoamylate* acted with tribromtrinitrobenzol in the same way as the alcoholates already mentioned, but the organic products insoluble in water were oily, and we did not succeed in isolating any compounds fit for analysis from them. The aqueous filtrates contained a considerable amount of the sodium salt of trinitrophloroglucin. As the subject was not of sufficient interest to repay extended work, it was abandoned.

Quantitative Study of the Action of other Alcoholates on Tribromtrinitrobenzol.

The object of this work was to make a comparison between the actions of sodic ethylate and of other alcoholates on tribromtrinitrobenzol, and for this purpose we selected the quantitative determination of the amounts of sodic nitrite formed by the reaction, since our results with the ethylate had shown that the percentage of nitrogen removed as sodic nitrite was essentially constant under the conditions used by us. The amount of bromide formed was also determined in most cases, although of little value for purposes of comparison. Accordingly the following determinations were made, the results of which, with those from sodic ethylate already described, are given together in tabular form after the descriptions of the determinations. To economize our alcohols, as we had but a small stock of some of them, we have used principally the method with benzol as a solvent.

Experiments in which the Alcohol was the only Solvent.

XIV. Weight taken, 1.0578 grams. Alcoholate used, *sodic methylate.* Weight of aqueous solution, 115.1 grams. 54.3 grams solution gave 13.6 cc. N from $NaNO_2$ at 18° and 758.9 mm. 60.8 grams solution gave 0.3768 gram AgBr.

XV. Weight taken, 1.157 grams. Alcoholate used, *sodic propylate.* Weight of aqueous solution, 92 grams. 54.1 grams solution gave 13 8 cc. N from $NaNO_2$ at 16° and 775.4 mm.

XVI. Weight taken, 1.1582 grams. Alcoholate used, *sodic isobutylate.* Weight of aqueous solution, 117.5 grams. 33.1 grams solution gave 5.25 cc. N from $NaNO_2$ at 16° and 765.5 mm. 43.3 grams solution gave 0.2390 gram AgBr.

XVII. Weight taken, 1.2696 grams. Alcoholate used, *sodic isobutylate.* Weight of aqueous solution, 56.65 grams. 19.3 grams solution gave 9.4 cc. N from $NaNO_2$ at 29.5° and 756.3 mm. 15.95 grams solution gave 0.2198 gram AgBr.

XVIII. Weight taken, 1.5118 grams. Alcoholate used, *sodic isoamylate.* Weight of aqueous solution, 53.3 grams. 26.5 grams solution gave 8.4 cc. N from $NaNO_3$ at 20° and 762.4 mm. 26.25 grams solution gave 0.3352 gram AgBr.

XIX. Weight taken, 1.5656 grams. Alcoholate used, *sodic isoamylate.* Weight of aqueous solution, 85.1 grams. 37.4 grams solution gave 9.9 cc. N from $NaNO_3$ at 19.5° and 766.2 mm.

Action of Sodic Methylate in Benzol.

XX. Weight taken, 1.0892 grams. Weight of solution, 65.7 grams. 31.7 grams solution gave 10.1 cc. N from $NaNO_3$ at 22° and 766.9 mm. 34 grams gave 0.4212 gram AgBr. Organic matter insoluble in water, 0.509 gram.

XXI. Weight taken, 1.2612 grams. Weight of aqueous solution, 40.05 grams. 17.35 grams solution gave 11.7 cc. N from $NaNO_3$ at 25° and 758.9 mm. 22.7 grams solution gave 0.4088 gram AgBr.

XXII. Weight taken, 1.1561 grams. Weight of aqueous solution, 58.9 grams. 24.3 grams solution gave 10.9 cc. N from $NaNO_3$ at 25.5° and 765.4 mm. 34.6 grams solution gave 0.4732 gram AgBr.

Action of Normal Sodic Propylate in Benzol.

XXIII. Weight taken, 1.2281 grams. Weight of aqueous solution, 60.85 grams. 22.75 grams solution gave 8.2 cc. N from $NaNO_3$ at 20.5° and 759.4 mm. 38.1 grams solution gave 0.1398 gram AgBr.

XXIV. Weight taken, 1.297 grams. Weight of aqueous solution, 71.6 grams. 19.6 grams solution gave 4.6 cc. N from $NaNO_3$ at 30° and 767 mm. 52 grams solution gave 0.7827 gram AgBr.

Action of Sodic Isopropylate in Benzol.

XXV. Weight taken, 1.3434 grams. Weight of aqueous solution, 50.15 grams. 20 grams solution gave 5.9 cc. N from $NaNO_3$ at 24.5° and 762.5 mm. 30.15 grams solution gave 0.2679 gram AgBr.

Action of Sodic Isobutylate in Benzol.

XXVI. Weight taken, 1.1598 grams. Weight of aqueous solution, 59 05 grams. 27.05 grams solution gave 5.2 cc. N from $NaNO_3$ at 23.5° and 759.2 mm. 32 grams solution gave 0.303 gram AgBr.

XXVII. Weight taken, 1.1551 grams. Weight of aqueous solu-

tion, 79.5 grams. 22.05 grams solution gave 4.2 cc. N from $NaNO_3$ at 27° and 764.5 mm. 57.45 grams solution gave 0.722 gram AgBr.

Action of Sodic Isoamylate in Benzol.

XXVIII. Weight taken, 1.4427 grams. Weight of aqueous solution, 85.55 grams. 31.7 grams solution gave 5.7 cc. N from $NaNO_3$ at 23° and 760.9 mm. 40.65 grams solution gave 0.4184 gram AgBr.

XXIX. Weight taken, 1.4485 grams. Weight of aqueous solution, 106.65 grams. 33.6 grams solution gave 5.3 cc. N from $NaNO_3$ at 25.5° and 764.2 mm. 73.05 grams solution gave 0.8515 gram AgBr.

Action of Sodic Benzylate in Benzol.

XXX. Weight taken, 1.0747 grams. Weight of aqueous solution, 92.2 grams. 33.5 grams solution gave 2.7 cc. N from $NaNO_3$ at 30.5° and 758.8 mm. 58.7 grams solution gave 0.5584 grams AgBr.

Action of Sodic Phenylate in Benzol.

XXXI. Weight taken, 1.1227 grams. Weight of aqueous solution, 67.15 grams. 32.5 grams solution gave 3 cc. N from $NaNO_3$ at 29° and 766.5 mm. 30.05 grams solution gave 0.1568 gram AgBr.

The results of these experiments are collected in Tables III and IV with those previously given by sodic ethylate. The first column contains the sort of alcohol used and the number of the experiment, the second the weight of tribromtrinitrobenzol used, the third the percentage of nitrogen, and the fourth the percentage of bromine removed, calculated in the way already described in connection with Tables I and II.

TABLE III.—*Experiments with the Alcohol alone.*

Sort of Alcohol used.		Weight of Tribromtrinitrobenzol.	Percentage of Nitrogen.	Percentage of Bromine.
Methyl	XIV	1.0578	50.52	53.79
Ethyl	I	10.556	45.88	42.53
	II	10.1582	44.85	36.67
	III	1.0366	46.95	42.85
	IV	10.	46.86	39.39
	V	10.	45.06	18.02
Propyl	XV	1.157	38.80	...
Isobutyl	XVI	1.1582	30.40	44.69
	XVII	1.2696	37.83	49.04
Isoamyl	XVIII	1.5118	20 62	36.16
	XIX	1.5656	26.73	...

TABLE IV.—*Experiments with Alcohol and Benzol.*

Sort of Alcohol used.		Weight of Tribromtrinitrobenzol.	Percentage of Nitrogen.	Percentage of Bromine.
Methyl	XX	1.089	35.28	59.62
	XXI	1.261	38.37	45.64
	XXII	1.156	41.17	55.59
Ethyl	VI	10.022	33.58	59.54
	VII	10.1976	33.09	38.91
	VIII	1.2524	33.03	74.32
	IX	1.2682	33.31	66.21
	X	1.2287	34.42	49.10
Propyl	XXIII	1.2281	32.74	14.51
	XXIV	1.297	22.83	66.30
Isopropyl	XXV	1.3434	19.87	26.46
Isobutyl	XXVI	1.1598	17.68	38.46
	XXVII	1.1551	23.41	69.01
Isoamyl	XXVIII	1.4427	19.33	48.70
	XXIX	1.4485	20.89	68.50
Benzyl	XXX	1.0747	12.00	65.09
Phenol	XXXI	1.1227	9.78	24.90

An examination of Tables III and IV shows that the percentages of nitrogen obtained with the ethylate are the only ones which agree among themselves, the numbers with other alcoholates often differing by about six per cent.—in one case by nearly ten per cent. Under these circumstances it is obviously unwise to attempt to draw any definite inferences from these results; we therefore dismiss them with the general remark that the amount of nitrogen removed seems to show a tendency to diminish as the molecular weight of the alcohol increases.

The length of time during which the mixture of tribromtrinitrobenzol and the alcoholate stood seemed to have but little influence on the reaction, as is shown by Experiments V, XXIV, XXVII, and XXIX, in which the mixture stood one or more days longer than the eighteen hours used for the other experiments. In fact, longer standing could not have any great effect in the case of the ethylate, as in eighteen hours eighty to ninety per cent. of the tribromtrinitrobenzol had entered into the reactions. With the higher alcoholates this was not the case, and it may be that the action had not reached its end in eighteen hours, and that the variation observed in the percentages was due to differences in the

times of reaction; but some experiments, in which the mixtures were allowed to stand a longer time in order to test this point, gave unsatisfactory results, apparently on account of the oxidation of the sodic nitrite formed by the oxygen of the air.

Part III.—Action of Sodic Ethylate on Certain Derivatives of Tribromtrinitrobenzol containing Alkyloxy Radicles.

Action of Sodic Ethylate on the Triphenyl Ether of Trinitrophloroglucin.

This work was undertaken in the hope that the triphenyl ether of trinitrophloroglucin, $C_6(OC_6H_5)_3(NO_2)_3$, might behave toward sodic ethylate like tribromtrinitrobenzol, that is, lose one or more nitro groups as sodic nitrite, which would be replaced by the ethoxy group. This hope, however, has not been fulfilled, as instead of the nitro groups the phenoxy radicles are removed by the sodic ethylate, becoming replaced by ethoxy groups, while sodic phenylate is formed. The experiments were carried on as follows: 2.5 grams of the triphenyl ether of trinitrophloroglucin[1] dissolved in benzol were mixed with the sodic ethylate from 0.4 gram of sodium, and the bright red mixture allowed to stand two or more hours in the cold. After this it was allowed to evaporate spontaneously, and the residue warmed with water on the steam-bath, when most of it dissolved. The insoluble portion was purified by crystallization from alcohol until it showed the constant melting-point 119°–120°, which indicated that it was trinitrophloroglucin triethyl ether, and this was proved to be the case by the following analysis:

0.2080 gram substance gave 22.5 cc. N at 21° and 759.3 mm.

	Calculated for $C_6(OC_2H_5)_3(NO_2)_3$.	Found.[2]
Nitrogen	12.17	12.30

The aqueous filtrate which contained the other products of the reaction besides the trinitrophloroglucin triethyl ether gave no

[1] In preparing this substance from tribromtrinitrobenzol again we have found that a tolerable excess of sodic phenylate should be used in order to avoid the formation of a compound containing bromine, — $C_6(OC_6H_5)_2Br(NO_2)_3$ probably. With such an excess, the reaction runs without heat, and is complete in a few minutes. We have not observed the green color noticed by us last year (this Journal **13**, 189), which must therefore have been due to some impurity.

[2] This analysis has also been given earlier in this paper, where the composition of the triethyl ether is first determined.

test for sodic nitrite, even with starch-paste, potassic iodide, and sulphuric acid. It was acidified with dilute sulphuric acid and extracted with ether, which left an oily substance solidifying after some time, and smelling strongly of phenol. To prove that this was phenol, it was dissolved in a large quantity of water and bromine-water added to the solution, which gave a white precipitate melting constantly, after crystallization from dilute alcohol, at 92°, the melting-point given by Post for tribromphenol; as, however, both Körner and Sintenis give 95°, we thought it necessary to analyze the substance, which was done with the following result:

0.2803 gram substance gave by Carius' method 0.4748 gram AgBr.

	Calculated for $C_6H_3Br_3OH$.	Found.
Bromine	72.51	72.07

There can be no doubt, therefore, that the substance is tribromphenol, and that the action of the sodic ethylate upon trinitrophloroglucin triphenyl ether takes place according to the following reaction:

$$C_6(OC_6H_5)_3(NO_2)_3 + 3NaOC_2H_5 = C_6(OC_2H_5)_3(NO_2)_3 + 3NaOC_6H_5.$$

The bright red color observed in the solution was undoubtedly due to some of the sodium salt of trinitrophloroglucin formed by the action of the small amount of sodic hydrate, which it is almost impossible to exclude from sodic ethylate owing to the hygroscopic nature of absolute alcohol.

This decomposition of the trinitrophloroglucin triphenyl ether by sodic ethylate calls to mind the behavior of esters with another alcohol and a small quantity of an alcoholate, as studied by Purdy[1] and Peters,[2] especially as our ether approaches the esters on account of the marked acid properties of the trinitrophloroglucin. Kossel and Krüger[3] have also found that sodic ethylate converts salol into salicylic ester (or acid), and sodic phenylate, and that glycerids are decomposed by sodic ethylate in a similar way, a result which is confirmed by Obermüller.[4]

Action of Sodic Ethylate on Tribromnitroresorcin Diethyl Ether.

Early in our work with the tribromnitroresorcin diethyl ether melting at 101° we noticed that, although it was not acted on by a

[1] Ber. d. chem. Ges. **20**, 1554.
[2] Ann. Chem. (Liebig) **257**, 353.
[3] Ztschr. physiol. Chem. **15**, 321.
[4] *Ibid.* **16**, 152.

cold solution of sodic ethylate in alcohol, it was attacked if heated with such a solution, but our attempts to study this reaction were baffled for a long time by the difficulty in removing from the crystalline product the large amount of tarry matter which was formed at the same time, even constituting almost the whole of the mass, if the heat was not applied cautiously. After many experiments we succeeded in obtaining a satisfactory result by proceeding as follows: 13 grams of tribromnitroresorcin diethyl ether were covered with absolute alcohol, and an alcoholic solution of sodic ethylate added. The flask containing the mixture was, after fitting it to a return-condenser, immersed in a beaker of cold water, which was heated slowly. As the temperature rose the substance went into solution with a pale reddish color, and in a few minutes after that there was a sudden change, the solution becoming almost black, although the reaction was not at all violent. At this point the heating must be stopped to avoid the formation of a large quantity of the tarry impurity. The contents of the flask, which had a peculiar aromatic odor not belonging to the compound we have isolated, was allowed to evaporate to dryness spontaneously, and the residue washed several times with cold water, which was found to contain sodic bromide. The water left undissolved a most unpromising tarry mass with almost no sign of crystalline form, but by extracting it with hot ligroïn a crystalline substance was obtained, which was purified by repeated crystallization from hot alcohol with the aid of bone-black until it melted constant at 115°, when it was dried at 100° and analyzed with the following results:

I. 0.1897 gram substance gave 0.2874 gram CO_2 and 0.0782 gram H_2O.

II. 0.1519 gram substance gave by Carius' method 0.0985 gram AgBr.

	Calculated for $C_4H_2BrNO_2(OC_2H_5)_2$.	Found. I.	II.
Carbon	41.38	41.31	...
Hydrogen	4.14	4.58	...
Bromine	27.58	...	27.60

The substance has therefore been formed from the tribromnitroresorcin diethyl ether by the replacement of two atoms of bromine by two of hydrogen, a reaction which is similar in principle to the replacement of the bromine by hydrogen in bromdinitroresorcin

diethyl ether, when treated with a boiling solution of sodic ethylate in alcohol, and to the similar replacements of bromine by hydrogen in the formation of bromdinitrophenylmalonic ester and related substances from tribromdinitrobenzol and tribromtrinitrobenzol.

Properties of Bromnitroresorcin Diethyl Ether, $C_6H_2BrNO_2(OC_2H_5)_2$.

The substance crystallizes from hot alcohol in long radiating silky white needles, which melt at 115°, and are soluble in cold alcohol, more freely in hot; freely soluble in cold methyl alcohol; very freely in benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ligroïn, much more soluble in hot; essentially insoluble in water. Neither hydrochloric, nitric, nor sulphuric acid seems to have any action on it, and the same is the case with a solution of sodic hydrate.

LXXX.—ON THE CUPRIAMMONIUM DOUBLE SALTS.[1]

By Theodore William Richards and Hubert Grover Shaw.

In the course of an extended investigation upon the ammoniacal compounds of copper, undertaken with the hope of obtaining more light upon the vexed question of their structure, a new class of interesting compounds was discovered. The preliminary notice of these compounds was published about a year ago;[2] but since that time several new ones have been added to the list. It is the object of this paper more fully to describe all of these substances, so far as they have been studied.

The generic feature of the new class is the fact that two different acids—a halogen and an organic acid radicle—are united at the same time to the ordinary cupriammonium group. Below are tabulated the formulæ of the compounds, the preparation, properties, and analyses of which are described in the work which follows:

(1.) $Cu(NH_3)_3BrC_2H_3O_2$.
(2.) $Cu(NH_3)_3ClC_2H_3O_2.H_2O$.
(3.) $[Cu(NH_3)_3ClC_2H_3O_2]_2.3NH_4C_2H_3O_2 + 7H_2O$.
(4.) $Cu(NH_3)_3BrCHO_2$.

[1] Presented at a meeting of the American Academy of Arts and Sciences, held May 10, 1893.

[2] Theodore W. Richards: Ber. d. chem. Ges. **25**, 1492. Since the publication of this paper, F. Foerster has announced the discovery of cupriammonium acetate (*Ibid.* **25**, 3416).

Besides these compounds two others, which appeared as by-products of the investigation, are worthy of description:

(5.) $CuCl_2.2NH_4C_2H_3O_2$.

(6.) $3CuBr_2.10NH_3$.

1. *Cupriammonium Acetobromide*, $Cu(NH_3)_2BrC_2H_3O_2$.—This compound is formed with great ease whenever cupric bromide is treated with alcohol and saturated with ammonia-water, and the mixture is nearly neutralized with strong acetic acid. For example, 5 grams cupric bromide were shaken with 10 cc. alcohol and the like volume of saturated ammonia-water, until all of the copper was converted into cupriammonium bromide. The bright blue precipitate was then immediately dissolved in 60–70 cc. additional alcohol, and 16 cc. strong acetic acid. Upon cooling the solution, and allowing it slowly to evaporate in the air, large brilliant deep-blue crystals which apparently belong to the monoclinic system, slowly separated.[1]

The same substance may be obtained in a similar manner from cupric acetate and ammonic bromide, after treating with ammonia and afterwards with acetic acid.

The new compound is only very slightly soluble in pure alcohol, and is decomposed at once by water into impure cupric hydroxide, ammonic acetate and ammonic bromide. The cupric hydroxide contains large amounts of basic cupric bromide and acetate.

The only satisfactory solvent for it seems to be a strong aqueous solution of ammonic acetate and bromide, containing more or less alcohol. By this singular mixture the compound is not decomposed, even at 70° or 80° C. Acids of course at once decompose and dissolve cupriammonium acetobromide, and alkalies upon boiling set free ammonia and precipitate cupric oxide as usual. The crystals are fairly permanent in the air; they are singularly brittle and rather light, possessing a specific gravity of 2.134.

In the analysis of the compound, copper was determined electrolytically after evaporation with sulphuric and nitric acids; and the bromine and ammonia were determined as usual. The accurate determination of the acetic acid was a much harder task. Distillation with phosphoric acid, according to the method recommended by Fresenius,[2] is not very satisfactory because of the great expenditure of time which it requires, and the fact that

[1] T. W. Richards: Ber. d. chem. Ges. **23**, 3791.

[2] Zischr. anal. Chem. **5**, 315; **14**, 172.

traces of hydrobromic and phosphoric acids are always found in the distillate. Usually the two acids were precipitated together from the neutralized distillate, and the result was calculated as argentic bromide; but in some cases they were determined separately. The presence of phosphoric acid in the distillate is especially unfortunate, because of the uncertainty which it introduces in the end-point of the alkalimetric reaction.

On the other hand, quantitative combustion after the usual method, and calculation of the acetic acid from the carbon dioxide formed, is not easy because of the presence of the large amount of bromine.

Analyses of $Cu(NH_4)_2BrC_2H_3O_2$.

I. 0.0685 gram substance yielded 0.01865 gram Cu upon electrolysis.

II. 0.1446 gram substance distilled with KOH required 12.16 cc. decinormal acid solution for neutralization.

III. 0.08485 gram substance yielded 0.06705 gram AgBr.

IV. 0.3173 gram substance yielded 0.2518 gram AgBr.

V. The distillate from a mixture of phosphoric acid and 0.2311 gram substance required 10.11 cc. decinormal alkali for neutralization. Approximately corrected for alkalimetric equivalent of Ag_2PO_4 and AgBr obtained from distillate this amount becomes 9.90.

Many other analyses were made of subsequent preparations, in order to be sure of the identity of the crystals prepared in different ways. It is considered unnecessary to publish these, since they agreed essentially with those given above.

No.	Cu.	NH_3.	Br.	$C_2H_3O_2$.
I.	27.23	...	...	...
II.	...	14.35	...	...
III.	...	...	33.63	...
IV.	...	...	33.78	...
V.	...	...	...	25.27
Average,	27.23	14.35	33.70	25.27

	Calculated for $Cu(NH_3)_2BrC_2H_3O_2$.	Found (Mean).
Cu	26.87	27.23
NH_3	14.42	14.35
Br	33.79	33.70
$C_2H_3O_2$	24.92	25.27
	100.00	100.55

2. *Ammon-cupriammonium Acetochloride*, $Cu(NH_3)_3ClC_2H_3O_2.H_2O$.—Almost any mixture which brings together in concentrated solution copper, chlorine, much acetic acid, and an excess of ammonia yields ammon-cupriammonium acetochloride upon the addition of alcohol. The substance consists of brilliant blue scales, having a pearly luster. These crystals lose ammonia and water slowly upon exposure to the air, with marked alteration of color; they are decomposed by water, a small amount of the copper going into solution. For analysis the crystals were pressed between layers of filter-paper as rapidly as possible. A bromine compound similar in every respect to this one has been prepared, and will form the subject of a future communication.

Analyses of Ammon-Cupriammonium Acetochloride.

I. 0.2524 gram substance yielded on electrolysis 0.0698 gram Cu.

II. 0.2273 gram substance yielded 0.0634 gram Cu.

III. 0.2875 gram substance yielded 0.0808 gram Cu.

IV. 0.1337 gram substance required on distillation 17.37 cc. decinormal acid to neutralize ammonia volatilized.

V. 0.1554 gram substance required in the same way 20.17 cc. acid.

VI. 0.0979 gram substance required 12.56 cc. decinormal acid.

VII. 0.2708 gram substance yielded 0.1704 gram AgCl.

VIII. 0.2696 gram substance yielded 0.1700 gram AgCl.

IX. 0.1926 gram substance yielded upon distillation with phosphoric acid a distillate requiring 8.94 cc. decinormal baric hydroxide for neutralization with phenol phthalein. This liquid yielded 0.0116 gram AgCl, containing traces of Ag_3PO_4, which amount is equivalent to about 0.81 cc. decinormal acid. Hence the acetic acid in the distillate must have required 8.13 cc. alkaline solution.

X. 0.2215 gram substance required upon distillation 10.38 cc. baric hydrate, of which 0.66 were required to neutralize HCl corresponding to 0.0096 gram AgCl obtained from the neutralized distillate ($10.38 - 0.66 = 9.72$).

No.	Cu.	NH_3.	Cl.	$C_2H_3O_2$.
I.	27.65	...	...	...
II.	27.89	...	...	...
III.	28.17	...	...	...
IV.	...	22.16	...	...

No.	Cu.	NH_3.	Cl.	$C_2H_3O_2$.
V.	...	22.14	...	...
VI.	...	21.89	...	...
VII.	...	...	15.56	...
VIII.	...	...	15.59	...
IX.	...	...	...	24.91
X.	...	...	...	25.90
Average,	27.90	22.06	15.57	25.40

The averaged results are given below.

	Calculated for $Cu(NH_3)_2ClC_2H_3O_2H_2O$.	Found.
Cu	27.98	27.90
NH_3	22.53	22.06
Cl	15.60	15.57
$C_2H_3O_2$	25.97	25.40
H_2O (by difference)	7.92	9.07
	100.00	100.00

3. *Complex*[1] *Cupriammonium Acetochloride*, $[Cu(NH_3)_2ClC_2H_3O_2]_2.3NH_4C_2H_3O_2 + 7H_2O$.—The complex cupriammonium acetochloride is obtained under conditions which would have been expected to produce the simple compound enclosed in the brackets above. This simple compound, probably owing to its great solubility, we have been unable as yet to isolate. Whenever cupric chloride is treated with a great excess of concentrated ammonia-water, the excess cautiously neutralized with glacial acetic acid, and the whole treated with alcohol and allowed to evaporate, great crystals of the complicated compound containing three molecules of ammonic acetate and probably seven of water to every two of cupriammonium acetochloride always separate out. The addition of somewhat more acetic acid in this case constitutes the sole difference between the methods of preparing this compound and the preceding. In the former case an excess of ammonia was required.

The crystals of the complex salt are of a most brilliant blue with a tinge of violet, and may be obtained of almost any size. They dissolve in very small amounts of water without apparent decompo-

[1] "Complex" is used here in default of a word more capable of describing the complexity of the compound. It is not intended to carry with it any technical meaning with regard to the structure of the molecule. Indeed, the names of all the compounds described in this paper are far from satisfactory to us; they would be thrown out very gladly if better ones could be found.

sition, but larger amounts of water decompose them. The new compound readily loses water and ammonic acetate in the air, and is converted into a pale green powder, which remains to be investigated. Over caustic potash in a desiccator, on the contrary, it is soon converted into a pale violet powder with a very sudden loss of weight. After the sudden decrease has stopped a slower decrease continues, without change of color, and the composition of the powder constantly approaches that of the simple cupriammonium acetochloride. Its complete conversion into this compound we have not yet been able to accomplish; and regarding the exact nature of the compounds which are marked by the irregular decrease in weight we have as yet nothing to say.

For analysis the crystals were pressed between layers of filter-paper. The possible causes of error from decomposition on the one hand, and the adhesion of mother-liquor on the other, were guarded against as much as possible. Nevertheless these causes of error are undoubtedly responsible for the not unreasonable variations noticeable in the analytical results; for the three specimens of crystals analyzed were undoubtedly identical.

Analyses of Complex Cupriammonium Acetochloride.

I. 0.2404 gram substance yielded on electrolysis 0.0411 gram Cu.

II. 0.2446 gram substance yielded on electrolysis 0.0419 gram Cu.

III. 0.2772 gram substance yielded on electrolysis 0.0476 gram Cu.

IV. 0.1418 gram substance yielded on distillation $NH_3 = 13.25$ cc. decinormal acid.

V. 0.1403 gram substance required on distillation 13.24 cc. decinormal acid.

VI. 0.1895 gram substance required on distillation 17.79 cc. decinormal acid.

VII. 0.1472 gram substance required on distillation 14.19 cc. decinormal acid.

VIII. 0.2319 gram substance yielded 0.0895 gram AgCl.

IX. 0.2244 gram substance yielded 0.0870 gram AgCl.

X. 0.1679 gram substance gave on combustion 0.0998 gram CO_2.

No.	Cu.	NH_3.	Cl.	$C_2H_3O_2$.
I.	17.10	...	...	...
II.	17.13	...	...	...
III.	17.17	...	...	...
IV.	...	15.95	...	...
V.	...	16.11	...	...
VI.	...	16.03	...	...
VII.	...	16.46	...	...
VIII.	...	...	9.54	...
IX.	...	...	9.59	...
X.	...	...	...	39.95
Average,	17.13	16.16	9.57	39.95

	Calculated for $Cu_2(NH_3)_4Cl_2(C_2H_3O_2)_2(NH_4)_2.7H_2O$.	Found (Mean).
Cu	17.12	17.13
Cl	9.55	9.57
NH_3	16.08	16.16
$C_2H_3O_2$	39.73	39.95

A fourth sample, which had a similar appearance, was found to contain 17.61 per cent. of copper and 9.94 of chlorine. This had probably begun to lose water and ammonic acetate. A finely powdered specimen kept for eleven months over sodic hydrate was found to contain 25.8 per cent. of copper and 14.35 of chlorine. Since the theoretical percentages corresponding to $Cu(NH_3)_2ClC_2H_3O_2$ are respectively 33.08 and 18.45, it is clear that the excess of ammonic acetate had not been wholly decomposed during the long exposure. Further experiments in this direction will be made in the near future.

4. *Cupriammonium Formibromide*, $Cu(NH_3)_2BrCHO_2$.—Cupriammonium formibromide is made after a method essentially similar to that employed in making the corresponding compound of acetic acid. The salt is more difficult to obtain in a pure state; but any reasonably concentrated solution containing bromine, copper, much formic acid, and ammonia in very slight excess, will deposit the deep "robin's-egg" blue crystals of the desired salt upon the addition of alcohol. The possibility of the formation of basic salts of copper is diminished if the excess of ammonia is added after the addition of the alcohol. The salt possesses no unexpected properties, except that the color of the short needles

is much less briliant and crude than that of cupriammonium acetobromide.

A similar compound containing chlorine instead of bromine has been prepared, and analyzed with results which were sufficiently accurate to show the analogy of the compound; but it was thought desirable to study more carefully the conditions necessary for its preparation in a pure state before publishing the results. Moreover, a more complex formibromide of most interesting aspect and composition has been made. This substance also awaits further study.

Analyses of Cupriammonium Formibromide.

I. 0.2192 gram substance gave on electrolysis 0.0621 gram Cu.

II. 0.2164 gram substance yielded on electrolysis 0.0618 gram Cu.

III. 0.1386 gram substance yielded $NH_3 = 12.32$ cc. of decinormal acid.

IV. Similarly 0.1180 gram substance required 10.46 cc. decinormal acid.

V. 0.1599 gram substance gave 0.1371 gram AgBr.

VI. 0.2414 gram substance gave 0.2063 gram AgBr.

VII. 0.1678 gram substance gave 0.1429 gram AgBr.

VIII. 0.2062 gram substance yielded on combustion 0.0403 gram CO_2.

IX. 0.2435 gram substance yielded on combustion 0.0469 gram CO_2.

No.	Cu.	NH_3.	Br.	CHO_2.
I.	28.30	...	...	...
II.	28.56	...	...	...
III.	...	15.17	...	...
IV.	...	15.13	...	...
V.	...	...	36.49	...
VI.	...	...	36.37	...
VII.	...	...	36.24	...
VIII.	...	...	...	19.93
IX.	...	...	...	19.70
Average,	28.43	15.15	36.37	19.80

These analyses were made from several different samples (especially V, VI, and VII, which were all different), and hence they

prove the definiteness of the compound. The average results are given below.

	Calculated for $Cu(NH_3)_2BrCHO_2$.	Found.
Cu	28.56	28.43
NH_3	15.33	15.15
Br	35.90	36.37
CHO_2	20.21	19.80
	100.00	99.75

5. *Cupric Ammonic Acetochloride*, $CuCl_2.2NH_4C_2H_3O_2$.—Upon several occasions during the investigation just described, when concentrated solutions of approximately equivalent amounts of cupric chloride and ammonic acetate had been allowed to evaporate together, especially with addition of alcohol, bright green, almost cubical, crystals separated. These crystals were sometimes found to be mixed with small amounts of ammonic chloride, and sometimes almost pure. The substance is a double salt, and not a cupriammonium compound; hence it dissolves in water without apparent decomposition. The purest crystals gave the following analytical results:

I. 0.3132 gram substance gave 0.0689 gram Cu.

II. 0.2649 gram substance gave 0.0585 gram Cu.

III. 0.1180 gram substance gave 0.1181 gram AgCl.

IV. 0.2091 gram substance gave 0.2150 gram AgCl.

V. 0.2121 gram substance yielded NH_3 = 14.47 cc. decinormal acid.

VI. 0.2158 gram substance required 14.20 cc. acid.

VII. 0.1930 gram substance required 13.83 cc. acid.

VIII. 0.2648 gram substance gave 0.1633 gram CO_2.

No.	Copper.	Chlorine.	Ammonium.	$C_2H_3O_2$.
I.	22.00	...	...	...
II.	22.09	...	...	...
III.	...	24.75	...	...
IV.	...	25.35	...	...
V.	...	...	12.34	...
VI.	...	. .	11.88(?)	...
VII.	...	...	12.98	...
VIII.	...	...	...	41.35
Average,	22.05	25.05	12.40	41.35

	Calculated for $Cu(NH_4)_3Cl_3(C_2H_3O_2)_2$.	Found.
Cu	22.03	22.05
Cl	24.56	25.05
NH_4	12.52	12.40
$C_2H_3O_2$	40.89	41.35
	100.00	100.85

6. *Tetrammon-Tricupriammonium Bromide*, $3Cu(NH_3)_2Br_2 4NH_3$.—Long ago Rammelsberg[1] described two compounds of ammonia and cupric bromide, to one of which, consisting of dark green crystals, he ascribed the formula $CuBr_2.3NH_3$; and to the other, consisting of a bright blue powder, he ascribed the formula $CuBr_2.5NH_3$. Recent investigation[2] has shown that the latter of the two substances must have been in reality $CuBr_2.6NH_3$, which had lost some of its very loosely combined ammonia by exposure to the air. The same investigation brought to light an olive-green substance having the formula $Cu(NH_3)_2Br_2$.

Repeated attempts were made at the same time to obtain Rammelsberg's first substance. The product of these trials invariably consisted of deep indigo, almost black, crystals, which contained noticeably more ammonia than the amount required by Rammelsberg's formula. These deep blue crystals are best obtained by adding, very cautiously, strong hydrobromic acid to a mixture of cupric bromide, alcohol, and just enough *aqua ammonia* to keep all the copper in solution. Upon the addition of enough acid to neutralize the ammonia, the crystals—which are almost insoluble in alcohol—begin to form.

Upon exposure to the air in a moist state these crystals lose ammonia rather rapidly; but when dry they are much more stable. Gentle heat (160°) readily converts them completely into the olive-green $Cu(NH_3)_2Br_2$, which still retains the crystalline form of the more complex salt. It is not impossible that Rammelsberg's green crystals consisted originally of the indigo-colored substance, which had lost superficially a little of its ammonia.

Tetrammon-tricupriammonium bromide is decomposed by water, a noticeable amount of copper going into solution in the form of a soluble compound containing proportionally more ammonia than the original substance. The reaction which takes place may possibly be represented somewhat as follows:

$$Cu_3(NH_3)_{10}Br_6 + 4H_2O = [Cu(NH_3)_6Br_2 + 4NH_4Br + Aq] + 2Cu(OH)_2.$$

[1] Ann. der Phys. Pogg. **55**, 246. [2] T. W. Richards: Ber. d. chem. Ges. **23**, 3790.

The amount of water present undoubtedly determines to a large extent the exact nature of the cupriammonium compound which remains undecomposed.

A great number of analyses of the indigo salt were made; partly because of the unusual nature of the formula which they indicated; and partly because the crystals, constantly appearing under many varying conditions in the work which has just been described, needed identification.

Analyses of $Cu_5(NH_3)_{10}Br_4$.

I. 0.4730 gram substance yielded 0.1075 gram Cu.
II. 0.4540 gram substance yielded 0.1033 gram Cu.
III. 0.2614 gram substance yielded 0.0594 gram Cu.
IV. 0.4269 gram substance yielded 0.5721 gram AgBr.
V. 0.4084 gram substance yielded 0.5476 gram AgBr.
VI. 0.2884 gram substance yielded 0.3861 gram AgBr.
VII. 0.1776 gram substance yielded NH_3 = 20.67 cc. decinormal acid.
VIII. 0.1245 gram substance required 14.77 cc. same acid.
IX. 0.1099 gram substance required 12.71 cc. same acid.
X. 0.1288 gram substance required 15.20 cc. same acid.
XI. 0.1175 gram substance required 13.85 cc. same acid.

No.	Copper.	Bromine.	Ammonia.
I.	22.73	...	...
II.	21.75	...	...
III.	22.72	...	...
IV.	...	57.03	...
V.	...	57.06	...
VI.	...	56.97	...
VII.	...	...	19.86
VIII.	...	...	20.25
IX.	...	...	19.74
X.	...	...	20.14
XI.	...	...	20.19
Average,	22.73	57.02	20.06

	Calculated for $CuBr_2.3NH_3$.	Calculated for $(CuBr_2)_3(NH_3)_{10}$.	Found (Mean).
Cu	23.15	22.68	22.73
Br	58.21	57.03	57.02
NH_3	18.64	20.29	20.06
	100.00	100.00	99.81

It is evident that this paper is merely an introduction to the possibilities in the direction indicated. Not only have other compounds of the same acids been already discovered, but many other acids, notably hydriodic, lactic, sulphocyanic, etc., show that they are capable of forming similar compounds. Moreover, the substituted ammonias may apparently take the place of the simple substance in most of the compounds. A few of these preparations are to be seen in the University exhibit at the World's Columbian Exhibition. The study of all these interesting substances will be continued in the immediate future at this Laboratory.

Contributions from the Chemical Laboratory of Purdue University.

VIII.—THE ACETYL AND BENZOYL DERIVATIVES OF THE PENTOSES.

By W. E. Stone.

Compounds between the better-known sugars (hexoses) and the acetyl and benzoyl radicles have frequently been prepared, and have served to throw light upon the constitution of the former. Theoretically all of the hydroxyl groups of the sugar are supposed to be replaced by the radicles in question, but in practice a complete substitution often fails to be attained. Thus di-, tri-, and tetracetyl compounds of dextrose have been obtained, as well as the pentacetyl dextrose corresponding to the accepted constitution of the latter. The same is true of the other hexoses (galactose and levulose) and of the disaccharides (sucrose, maltose, and lactose). In the same way benzoyl derivatives of the sugars have also been prepared, but these are even less constant in their composition than the corresponding acetyl compounds.

Similar derivatives of the two pentose sugars, arabinose and xylose, have not been prepared, and while the proofs of the constitution of these sugars have been well established by the researches of Kiliani and Fischer, it was still of interest to investigate their behavior in this particular.

Acetyl Derivatives.

Acetyl derivatives of bodies containing hydroxyl groups are as a rule easily formed by Liebermann's method,[1] which consists in heating the water-free substance with acetic anhydride and fused sodium acetate.

Both of the pentoses readily form tetracetyl derivatives corresponding to their accepted constitutions as tetroxy-aldehydes. These compounds have the formula $C_5H_6O_5(CH_3.CO)_4$, and characteristic properties of insolubility, bitter taste and optical activity. No product was obtained containing less than four acetyl radicles.

Tetracetylxylose. — 3 grams of pure xylose $[(\alpha)_D = 18.5°]$ obtained from straw, with 3 grams of freshly fused sodium acetate and 21 cc. of redistilled acetic anhydride, were placed in a flask attached to a reflux-condenser, and heated in a glycerol-bath during one hour at 105° C.

The reaction was attended by slight foaming at 80° to 90°, but was otherwise unmarked. On cooling the mass and adding ice-water in small quantities, there remained a pale-yellow, heavy oil, which after agitation and cooling crystallized as white shining scales. This product weighed upon drying 3.350 grams. It was soluble in warm alcohol, from which it recrystallized with difficulty, and was easily soluble in ether and benzene. It was quite insoluble in cold water, but dissolved easily on warming to 90°, from which solution it recrystallized on cooling in fine needles. The entire amount was recrystallized in this way.

This tetracetylxylose was bitter to the taste; indifferent toward Fehling's solution until after boiling some time, and melted sharply at 123.5°–124.5° without decomposition. A solution in absolute alcohol showed the specific rotation $(\alpha)_D = -25.43°$, without multirotation. Its composition was determined by saponifying and distilling off the free acetic acid. 0.250 gram was placed in a flask, and 50 cc. of water and 25 cc. ½-normal sulphuric acid added. About 50 cc. were distilled off directly, and then the distillation was continued at constant level by means of steam, until the distillate gave no further reaction upon litmus-paper. The distillate was then titrated with ½-normal sodium hydroxide, with the following results:

[1] Ber. d. chem. Ges. **11**, 1619.

	Taken.	Acetic Acid found.	Calculated for $C_5H_6O_5(CH_3CO)_4$.
I.	0.250 gram.	0.1848 gram.	0.1886 gram.
II.	0.250	0.1877	...
III.	0.250	0.1874	...

Tetracetylarabinose.—This was prepared in the same way as described above, but the oily insoluble body remaining after treatment with ice-water refused to crystallize, even when kept at —15° C. for some hours and frequently agitated. It was carefully separated from water and dissolved in absolute alcohol, in which it was easily soluble. This was, after filtration, set aside to evaporate. After drying three weeks over sulphuric acid there remained a dense transparent syrup of pale yellow color. From 3 grams of arabinose, 2.722 grams of this compound resulted. It had the same bitter taste as the xylose derivative; it was insoluble in water, save at high temperature, when it seemed to decompose; it reduced Fehling's solution after heating a short time. A portion was congealed by the use of solid carbon dioxide and ether, and the temperature of the melting mass remained constant at —7.6° for some time. In alcoholic solution it possessed the specific rotation $(a)_D = +26.39$. Upon saponification as already described, the following results were obtained:

	Taken.	Acetic Acid found.	Calculated for $C_5H_6O_5(CH_3CO)_4$.
I.	0.2773 gram.	0.2018 gram.	0.2091 gram.
II.	0.1489	0.1074	0.1121
III.	0.3298	0.2402	0.2489

These numbers conform less closely to the theoretical than those for the xylose derivative, but it was hardly possible to bring the arabinose compound to a high degree of purity. Both were undoubtedly tetracetyl derivatives. That their specific rotations were practically equal, but in opposite directions, was at least a noticeable coincidence.

Benzoyl Derivatives.

According to the method proposed by Baumann,[1] benzoyl chloride reacts upon the sugars, forming benzoyl esters in which the hydrogen atom of each hydroxyl group of the sugar is replaced by the benzoyl radicle.

Baumann's method has been somewhat modified by Panormoff,[2] but it seems to be the common experience that the theoretical

[1] Ber. d. chem. Ges. **19**, 3220. [2] Chem. Centralb. 1891, **2**, 853.

reaction does not always occur. At least the derivatives thus obtained from the sugars are of variable composition, and Ruenz[1] intimates that such products are not single compounds, but mixtures of more or less complete esters.

To 1 part of xylose dissolved in water were added 160 parts of 10-per cent. sodium hydroxide solution and 18 parts of benzoyl chloride, and the whole thoroughly shaken together for a quarter-hour. A foamy substance gradually formed on the surface of the liquid, which upon standing became firm and tenacious, and on cooling was brittle. Arabinose treated in the same way yielded a similar product. Both preparations were washed with warm water and dissolved with hot alcohol, from which they were again precipitated by water. They were again redissolved in hot alcohol, and left to crystallize by slow evaporation. The xylose derivative crystallized slowly in large pointed crystals. The arabinose compound separated more rapidly as oily colorless drops which refused to crystallize. It was redissolved in hot alcohol, and, by addition of pieces of ice, was thrown down as an amorphous flocculent precipitate.

Both products were entirely odorless and tasteless. They were without effect upon boiling Fehling's solution. The benzoylxylose melted at 164°–165°; the arabinose derivative at 68°–69°; both were free from ash and chlorine. Analyses, however, failed to give any numbers corresponding to the calculated values for any single benzoyl derivative of a pentose. They were undoubtedly mixtures of different compounds.

The above results show that these pentoses behave like the other sugars in this respect, as has already been proved in regard to other reactions, while the introduction of four acetyl groups sustains the constitution already assigned them as tetroxyaldehydes.

IX.—THE ELECTROLYTIC OXIDATION OF GLYCEROL.

By W. E. Stone and H. N. McCoy.

The action of an electric current upon dilute solutions of glycerol has been studied by Rénard,[2] who noted formic, acetic, oxalic, and glyceric acids as well as simple and polymeric trioxy-

[1] Ztschr. physiol. Chem. **14**, 330. [2] Ann. chim. Phys. [5], **17**, 303.

methylene as products when the electrolyzed solution was acidulated with sulphuric acid. Bartoli and Paspagoli[1] observed under the same conditions, acroleïn, formic and glyceric acids, and trioxymethylene.

Lately E. Fischer[2] has shown that glycerol is oxidized to glyceral by the action of bromine, and with the glyceral thus obtained he accomplished the synthesis of glucose. We have attempted a similar partial oxidation of glycerol by the action of weak electric currents upon dilute solutions, and have succeeded in obtaining in this way small quantities of glyceral, but in general the action of even a weak current seems to accomplish complete oxidation of the alcohol in question, so that glyceral is only a transitory and intermediate product of the operation and ordinarily would elude observation.

We have studied the subject under varying conditions, the results of which will be summarized here. The apparatus employed was simple, consisting of one or two large bichromate-cells connected with electrodes of platinum, of an area of about 1½ square inches, which were submerged in the solutions to be studied. The strength of the current was measured by a Bunsen voltameter and was always less than 0.3 ampère. As glycerol is a non-conductor of electricity, it was necessary to add to the solution some conductor, which at the same time served to render the solution respectively acid, alkaline, or neutral, in reaction, and this in turn was found to have a decided influence upon the character of the products obtained. The solutions were usually made up of 20–25 grams of glycerol diluted to 200 cc. with water.

Oxidation of an Acid Solution.—A 10-per cent. solution of glycerol slightly acidulated with sulphuric acid and subjected to the action of a current of 0.2–0.3 ampère shows a rise in temperature, presently becomes able to produce a strong reduction of Fehling's solution *in the cold*, and to give the ordinary fuchsin-reaction for aldehydes. Later a perceptible odor of acroleïn is observed. The strong reduction of Fehling's solution in the cold is characteristic of glyceral. Eventually more or less of the glycerol becomes converted into acids, according to the duration of the action, but at no time was it possible to isolate any glyceral.

Oxidation in a Neutral Solution.—As a conductor 0.2 gram of sodium nitrate was used in 200 cc. of a 10-per cent. glycerol solu-

[1] Gaz. chim. Ital. **13**, 287. [2] Ber. d. chem. Ges. **20**, 3385.

tion. An acid reaction is soon noticeable—due to the formation of acids from the glycerol—and from this point the results were like those when free sulphuric acid was present; the solution gives a strong reduction with Fehling's solution in the cold, gives the fuchsin-reaction and smells of acrolein.

Oxidation in an Alkaline Solution.—A small quantity of sodium hydroxide was added to a 10-per cent. solution of glycerol, which was then electrolyzed as above. The first visible result was the appearance of a yellow color in the solution, which after some hours disappeared and then it was found that the solution was acid in reaction. In another trial 5 per cent. of sodium hydroxide was used and the yellowish brown color was very noticeable, but disappeared upon subsequent acidulation with acetic acid. Several oxidations were made in which a known amount of alkali and a known amount of glycerol were employed, and by subsequent titration it was found in all cases that a large amount of acid had been formed. In one case the acid amounted to 80 per cent. of the glycerol employed. These solutions also had the property of reducing Fehling's solution in the cold, but no odor of acrolein was perceptible.

The conclusions drawn from these general experiments were that glycerol is very susceptible to the action of electrolytic oxygen; that, first, a body with the property of an aldehyde is formed and is at once farther oxidized to an acid. The noticeable yellow color in the electrolyzed alkaline solution seemed explainable by the fact, as shown by Fischer, that glyceral, $C_3H_6O_3$, is easily polymerized in the presence of an alkali to glycerose (or glucose), $C_6H_{12}O_6$, and it is well known that the latter in contact with alkalies takes on a yellow color. In the above case it would seem that the glyceral, as formed, was polymerized to glycerose. This suggested a means of removing the glyceral from farther oxidation.

A weak current of less than 0.1 ampère was passed through an 8-per cent. solution of glycerol to which 0.5 per cent. of sodium hydroxide had been added, for a period of six days. The electrolytic cell and contents were kept cool (20° C.) by running water. The alkali was renewed once. A yellow color soon appeared in the solution and a strong reduction of Fehling's solution was produced in the cold. The filtrate from such a test, which gave no farther reaction in the cold, reduced still more strongly on boiling,

indicating a partial polymerization of the aldehyde. At the expiration of six days the current was interrupted, 2 per cent. more sodium hydroxide added and the whole placed in the cold during four days. The yellow color in the meantime became intensified, but the power to reduce Fehling's solution in the cold disappeared entirely, while the reduction on boiling was markedly increased. All of this pointed to the formation and polymerization of glyceral. In order to prove the presence of this polymeric product, glycerose, resort was had to the characteristic phenylhydrazine compound and to the fermentation-test. The alkaline solution was carefully neutralized and one-half was treated with phenylhydrazine chloride and sodium acetate in the usual way. The solution, after heating in boiling water for six hours, on cooling threw down a voluminous golden yellow precipitate. This, after repeated recrystallization from benzene and ethyl acetate, melted at 200° C. The quantity did not admit of further purification. The melting-point of glycerosazone was found by Fischer to be 204°.

The second portion of the solution above described was placed in contact with fresh brewers' yeast alongside of a blank containing only yeast and water. A lively fermentation began at once in the electrolyzed solution and continued normally until 25–30 cc. of carbon dioxide gas had been collected. No fermentation occurred in the blank sample. This result as well as the character of the phenylhydrazine derivative leaves no doubt as to the formation of an appreciable quantity of glyceral by the action of a weak current upon an alkaline solution of glycerol under such conditions as to facilitate polymerization of the former.

Glyceric Acid and its Optically Active Modification.

Glyceric acid, $C_3H_6O_4$, results as one of the products of the electrolytic oxidation of glycerol. It may be prepared more readily, however, by the oxidation of glycerol by nitric acid.[1] A more recent method suggested by Börnstern,[2] involving the action of mercuric oxide upon glycerol in alkaline solution, is easy to carry out and yields a product of high purity. As prepared by any of these methods, glyceric acid is optically inactive, although it contains an asymmetric carbon atom, and according to the theory at present accepted should be optically active. Its inactivity is,

[1] Mulder: Ber. d. chem. Ges. **3**, 1902. [2] *Ibid.* **18**, 3357.

however, explained on the assumption that it consists of equal or compensating portions of active acids respectively dextro- and laevo-rotatory. Such has been shown to be the fact in the cases of the inactive racemic, malic, lactic, asparagic, mannonic, galactonic and other acids, the separation of which into their optically-active isomers has been accomplished in different ways. Indeed, by the fermentative action of certain organisms there have been obtained from glyceric acid both the dextro- and laevo-rotatory modifications. Lewkowitch,[1] by cultivating *Penicillium glaucum* upon neutral inactive ammonium glycerate obtained laevo-glyceric acid, while Frankland and Frew, by a similar decomposition of neutral inactive calcium glycerate, obtained dextro-glyceric acid.[2] A complete separation and identification of both the active forms from a single portion of the inactive glyceric acid has, however, not yet been accomplished, although several other of the inactive acids have been separated in this manner. We have attempted this operation with glyceric acid, studying its salts with the alkaline earths and with certain alkaloids, but thus far without success. Strychnine and cinchonine glycerates were prepared and subjected to fractional crystallization, but in no case after decomposing the fractions was the free acid active. In the same way fractional solution in a variety of solvents was employed, but also without positive result. It appears that the separation of this acid into its optical isomers presents greater difficulties than some others which have been thus resolved.

X.—THE CARBOHYDRATES OF THE FRUIT OF THE KENTUCKY COFFEE-NUT TREE (*GYMNOCLADUS CANADENSIS*).

By W. E. Stone and W. H. Test.

This tree, which occurs in fertile soils in the west and southwest of the United States, is closely related to the common thorny or honey locust (*Gleditschia*) and the European *Ceratonia siliqua*, the fruits of both of which are edible. The fruit of *Gymnocladus* resembles the others somewhat in appearance. It consists of a leathery pod of from three to ten inches in length, containing from two to six brown, oval and very hard seeds. These seeds are

[1] Ber. d. chem. Ges. 16, 2720.

[2] Trans. Chem. Soc. 1891, 96.

imbedded in a greenish waxy pulp or gum which possesses a sweet but also very disagreeable taste. This gum at the time of ripening is soft and easily removed, but later becomes hard and horny.

On account of the relation between this tree and those species producing the valuable commercial gums (gum arabic, gum copal, etc.), it was thought that this material (the gum) would repay investigation. Some preliminary tests showed the presence of an abundance of soluble reducing sugar and of pentosans (17 per cent.). The absence of galactose or galactan and of starch was also proven.

Forty of the seed-pods, collected in October, yielded 1300 grams of the fresh gum, which contained 52 per cent. of the moisture, leaving 675 grams of dry solid matter. This gum was extracted with 2500 cc. of boiling alcohol of 78-per cent. strength during six hours. This was filtered off and a second extraction made with 2000 cc. of alcohol of the same strength, also during a period of six hours.

In this way the sugars were dissolved and were removed by washing the insoluble gums on a filter until the washings gave no further reaction for sugar with Fehling's solution. The alcoholic extracts and the insoluble residue were examined separately.

The alcoholic extract was evaporated to a syrup and the impurities removed by the use of bone-black, precipitation with strong, hot alcohol, etc. Finally upon addition of a large volume of strong alcohol, a crop of fine white crystals was obtained, amounting to 20 grams in weight. These crystals consisted of a sugar, soluble in water, sweet, without direct effect upon Fehling's solution, but reducing strongly after inversion, and with a specific rotation $(\alpha)_D = 65.4°$, which after inversion became slightly laevo-rotatory. This sugar was therefore sucrose, of which, by continued crystallization, fully 100 grams were obtained. Taking into account the amount not recovered from the mother-liquor, this sucrose amounted to about 15 per cent. of the dry matter of the gum. There remained a large amount of uncrystallizable syrup, weighing about 130 grams, which contained a quantity of reducing sugar. From this a phenylhydrazine compound was prepared which melted at 203°, indicating glucose. The dry matter of the gum as taken from the seed-pod contained therefore about 15 per cent. of sucrose and an almost equal amount of glucose.

The gummy residue remaining after the soluble sugars had been extracted as above described was hydrolyzed by the action of 4000 cc. of 2-per cent. sulphuric acid at the temperature of boiling water during 12 hours. A portion of the material was dissolved, and a portion resembling cellulose remained behind. After filtration the solution was neutralized by calcium carbonate and concentrated by evaporation. After repeated attempts at purification there remained a thick, sweet syrup, which reduced Fehling's solution strongly, but refused to crystallize even on long standing. The furfurol-reaction revealed the presence of one of the pentoses. A phenylhydrazine compound melted at 175°–180°, which indicated a mixture of two or more sugars. A small portion of this compound was treated with just sufficient 95-per cent. alcohol to dissolve it at the boiling temperature; on cooling, a mass of fine yellow crystals separated, which melted sharply at 204°–205°, corresponding to the glucose derivative. On adding water to the filtrate, a yellow, flocculent mass was precipitated which melted at 140°–150°. This suggested a means of separating the phenylhydrazine compounds of the two sugars, which were evidently both present, by means of their different solubilities in water. Phenylxylosazon was found by actual experiment to be soluble in about 50 parts of boiling water, from which it separates on cooling. Phenylglucosazon, on the other hand, is quite insoluble in boiling water. The entire amount of the syrup was now converted into the phenylhydrazine compound, which weighed about 25 grams. A small portion of this, treated with 95-per cent. alcohol as already described, yielded a product melting at 204°–205° and containing no trace of a pentose, as shown by the furfurol-reaction. The larger portion of the mixture was boiled with 50 parts of water for two hours, upon which a considerable portion went into solution, was filtered off, and precipitated again on cooling. This was again recrystallized from hot water. The product thus obtained melted at 153° and gave an abundance of furfurol on heating with strong hydrochloric acid (the melting-points of both arabinosazon and xylosazon are 158°–160°). This may be taken as satisfactory proof of the presence of one of the pentoses. Its alcoholic solution was optically inactive, which distinguishes it from xylosazon, which has been shown to be active.

The insoluble gum of the fruit yielded, therefore, upon inversion, two sugars of distinctly different classes, a pentose (probably

arabinose) and a hexose (dextrose). It still remains a question if these were derived from separate mother-substances in the gum or from a single homogeneous substance, to which the name gluco-araban may be given, corresponding in its nature to the pentosans, galactan, etc. Such substances have been but sparingly noted. The first instance of the kind was recorded by one of us in the gum exuded from the bark and fruit of the peach-tree, which yields, on inversion, galactose and arabinose.[1] A similar galacto-araban has been noted in the coffee-bean[2] and in the seeds of certain leguminosae,[3] and a xylo-araban in the bran of wheat and rye.[3] This seems to be the first recorded observation of a gluco-araban.

In conclusion, the carbohydrates of the fruit of *Gymnocladus* seem to be remarkable in variety and abundance. Sucrose and glucose are both present in large quantities, while the insoluble portion contains bodies or a body which, on inversion, yields a pentose and glucose, to which the name of gluco-araban may be provisionally applied.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF SALTS ON ACIDS.

By R. W. Wood.

In Volume VIII, Number 3, of this Journal there appeared an article by J. R. Duggan, "On the determination of absolute neutrality." The author used diastase and starch as an indicator of neutrality, the presence of a small trace of acid or alkali inhibiting the action of the ferment. He found that in the case of weak acids a small amount of their neutral sodium salts prevented their inhibiting action on diastase, and in consequence he came to the conclusion that the salts must be alkaline. In the case of sodium acetate he found that 0.06 gram (2 equivalents) of acetic acid could be added to the starch in the presence of 0.02 gram (1 equivalent) of sodium hydrate, without affecting the diastase, while half this

[1] This Journal **12**, 435. [2] E. E. Elwell: This Journal **14**, 473.
[3] Schulze: Chem. Centralbl. 1892, **1**, 701.

amount of acid in the starch, no salt being present, would practically prevent all action of the ferment.

Sodium acetate he considered an alkaline salt, requiring the addition of another equivalent of acid to make it absolutely neutral. Such a solution is, however, strongly acid to other indicators, and the mere fact that its action on diastase is not inhibitory may not justify one in calling it neutral.

Duggan's work was done with great care; he examined various acids and salts and obtained interesting results, but there were several points that he overlooked in his investigations, which seem to show without question that some, at least, of the conclusions that he drew were erroneous.

The modern theory of dissociation seems to offer a better explanation of the phenomena, for the results of experiments seem to bear out the hypothesis that the inhibiting action on diastase is due to the free ions of hydrogen in the case of acids, and of hydroxyl in the case of alkalies. In the case of salts of weak acids it seems probable that part of the salt takes up water and dissociates into acid and base, the latter then being more fully dissociated into its ions, and the solution therefore acting like a base; on now adding an excess of acid this is dissociated, but not to the same extent as if no salt were present. When as many hydrogen ions as hydroxyl are formed in unit time, the solution no longer reacts on the diastase and we have what Duggan called absolute neutrality. The addition of more acid brings about action, though here again the restraining influence of the salt is felt.

When working under exactly the same conditions, the actions of salts and acids in varying proportion on diastase are so uniform that it seems highly probable that the method can be used for determining the amount of hydrolytic dissociation that occurs in salt solutions. The results given in this paper are not as accurate as it would be possible to obtain with specially constructed apparatus, for in certain cases very slight changes of temperature cause very wide variations. The work thus far has been essentially preliminary, there being many difficulties to overcome. Better results are expected in the continuation of the work with apparatus adapted to it. Duggan's work has been repeated, and enlarged upon to some extent, and the results seem to put the subject in a different light.

Materials and Methods.

The diastase was prepared by macerating finely ground pale barley-malt in distilled water for three hours, at the temperature of the room: the mush was squeezed in cloth bags, the fluid filtered to remove starch grains, and the diastase precipitated from the clear yellow solution by the addition of twice its volume of 95-per cent. alcohol. The precipitate was washed with absolute alcohol, dried in a vacuum over sulphuric acid, and very finely ground in an agate mortar. The product had a light brown color and was very energetic, converting about 75 times its weight of starch into maltose at 55° C. in thirty minutes. Duggan does not state how his diastase was prepared or how active it was. In his preliminary work he used commercial malt-extract, which is unsatisfactory. The starch was Taylor's preparation of Bermuda arrow-root, which was the purest that could be conveniently obtained.

2 grams of starch was found to be the best amount for each determination. It was stirred up in 5 cc. of water, and then added to 75 cc. of boiling water, forming a thin paste. The diastase was weighed each time to within 0.1 mg., 0.01 gram being the amount taken. It was stirred up with 10 cc. of water in a beaker, and put into a double-walled air-bath heated to 55° by boiling acetone. When the starch-paste had cooled down to about 60°, the acid or alkali or both were added by means of a graduated pipette, and when the temperature had fallen to exactly 55°, the paste was quickly poured into the beaker containing the diastase, and the air-bath quickly closed. The paste was stirred twice, once at the end of ten minutes, again at the end of twenty minutes, and at the expiration of thirty minutes the action was stopped by the addition of 2 cc. of a 10-per cent. solution of sodium hydroxide. The solution was then made up to 100 cc., and the sugar that had been formed determined volumetrically by Fehling's solution and reported as maltose.

Action of Acids and Alkalies on Diastase.

The action of sodium hydroxide was first tried, the determinations being made in a special room where the absence of fumes from the air could be assured. The alkali solution contained 0.8 gram of the base per liter. 1 cc. of this solution in 80 cc. starch-paste would correspond to ten parts of the alkali to one million of paste. The solution was made of this strength in order that the

results obtained might be compared with the results obtained by Duggan in his preliminary work. The following table indicates the action of varying amounts of alkali on 2 grams of starch and 0.01 gram diastase:

cc. of NaOH sol.	0	0.1	0.2	0.3	0.4
Parts to million	0	1	2	3	4
Maltose	0.739	0.674	0.639	0.616	0.508
cc. of NaOH sol.	0.5	1	1.5	2	
Parts to million	5	10	15	20	
Maltose	0.454	0.235	0.107	0.077	

This table shows that the diastase was much more sensitive than that used by Duggan: the smallest proportion of alkali that he detected was five parts to the million, whereas in this case one part gave a very perceptible retardation. A solution of phenolphthaleïn showed no trace of color until six parts of sodium hydroxide to a million of water were present. This shows how sensitive a substance diastase is. No other alkalies were tried.

The acids investigated were of the fatty series, and the solutions were all made equivalent to the alkali solution, by careful titration with phenolphthaleïn. Acetic acid gave the following results:

Acid, in cc.	0	0.5	0.75	1	1.5	2
Maltose, in grams	0.739	0.800	0.874	0.855	0.820	0.785
Acid, in cc.	3	4	5	7.5	10	20
Maltose, in grams	0.636	0.481	0.320	0.248	0.197	0.128

This series shows, what Duggan and others have found to be true, that a slight amount of acid has a favoring action, due probably to some impurity in the starch which, alone, exerts an inhibiting action, but is destroyed or neutralized by a small amount of acid. The effect of the acid is much less than that of an equivalent amount of alkali. Monochloracetic acid gave the following results:

Acid, in cc.	0.3	0.5	0.7	1
Maltose, in grams	0.785	0.874	0.835	0.810
Acid, in cc.	1.2	1.5	2	
Maltose, in grams	0.639	0.359	0.185	

which show that up to the point where the impurity in the starch is neutralized the stronger acid acts much like the weaker, but

when this point is passed, exerts a much more powerful action on the diastase. This was found to be true with all the acids tried, and seems to indicate that the impurity in the starch has the properties of an alkali and is neutralized by a certain definite equivalent of acid, wholly independent of the affinity of the acid. The action on the diastase depends on the nature of the acid as well as on the actual quantity. Dichloracetic and trichloracetic acids were tried, but did not give concordant results; the reason for this was subequently ascertained and will be referred to later. The other fatty acids retarded as follows:

Formic, in cc.	1	1.5	2
Maltose, in grams	0.547	0.296	0.173
Propionic	3	5	10
Maltose	0.592	0.320	0.184
Butyric	2	5	10
Maltose	0.854	0.320	0.128
Valeric	5	10	
Maltose	0.349	0.120	

These results are only *approximate*. It was found very difficult to get concordant results with any of the stronger acids. In the case of dichloracetic and trichloracetic acids this was at first thought to be due to the decomposition of the acids in solution, but as the same errors were found with perfectly stable acids, it seems probable that slight variations of temperature were responsible for the discrepancies. One determination with formic acid had given a yield of 0.290 gram maltose; a second gave 0.460 gram with the *same* amount of acid. It was thought that probably the small yield was due to the fact that the temperature was a little too low. Two determinations were made, taking scrupulous care to have the temperature exactly 55° (the most favorable one for diastatic action), and the yield in each case was 0.290 gram: *the smaller yield*. A determination was then made at 45° and the yield was found to be nearly 0.500 gram, showing that in the presence of an acid the most favorable temperature is much lower than when the acid is not present, or, in other words, that the power of the acid increases with the temperature to a much greater extent than the power of the diastase. With other acids the following effects were observed:

Acetic	Temp.	Maltose	Butyric	Temp.	Maltose
5 cc.	55°	0.305	10	55°	0.128
5	45°	0.470	10	45°	0.240

Valeric	Temp.	Maltose
5	55°	0.349
5	45°	0.577

This may be used for the determination of the effects of temperature on the action of the acids, and will be investigated later on. Very slight variations in temperature will produce very large variations in the results, and for this reason I do not attach much importance to the figures obtained with acids alone, since owing to the nature of the materials and apparatus it was difficult to be sure of the temperature within two degrees. The paste is with difficulty brought to a uniform temperature throughout, owing to its viscosity, and in pouring it suffers considerable loss of heat. The work is to be continued with a piece of apparatus designed for the purpose, in which six determinations can be made simultaneously, thereby ensuring similar conditions. The six beakers of starch are emptied into the six glasses containing the diastase by a mechanism operated from the outside of the closed chamber in which they are heated. Stirring-rods are kept in constant motion by a water-motor and the temperature can be kept constant within a quarter of a degree or less. The other results given in this paper may be considered fairly accurate, since very small variations in temperature, except in the presence of strong acid, seem to produce but little effect.

Action of Salts on their Acids.

It is from the results obtained in studying the action of salts on their acids that the most interesting theoretical deductions are to be drawn. Neutral salts of the weak acids above mentioned have a slight retarding effect, and in general the weaker the acid the greater the inhibiting action of its salt. Salts of strong acids, such as sodium chloride, have little or no effect on diastase.

Equivalent amounts of salt were used each time, *i. e.*, the quantity formed from 0.04 gram sodium hydroxide. In the case of sodium acetate this would give 0.082 gram of salt. In all the following cases 0.04 gram alkali is the amount used, and the retardation with one equivalent of acid is of course the retardation due to the neutral salt. The quantities of acid are given in equivalents:

Acetic,	1	$1\frac{1}{6}$	2	$2\frac{1}{2}$	3	5
Maltose,	0.662	0.874	0.874	0.874	0.8	0.4
Formic,	1	$1\frac{1}{16}$	$1\frac{1}{10}$	$1\frac{1}{5}$	$1\frac{2}{5}$	$1\frac{4}{5}$
Maltose,	0.6	0.874	0.874	0.8	0.385	0.115

Propionic,	2	3	4	5	6	8	10
Maltose,	0.874	0.874	0.874	0.828	0.55	0.4	0.16

Butyric,	1	$2\frac{2}{10}$	$2\frac{1}{2}$	3	4	6
Maltose,	0.481	0.874	0.74	0.693	0.427	0.18

Valeric,	1	3	4
Maltose,	0.481	0.662	0.427

It seems best to postpone a discussion of these figures with their theoretical bearing until fuller and more accurate results are obtained. It did not seem best to attempt with comparatively crude apparatus to make out very complete tables, since the object of the investigation thus far has been to obtain a general idea of the nature of the actions, rather than exact numerical results. In the case of the acetate, $\frac{1}{6}$ of an equivalent of acid in the presence of the salt gives the maximum yield of sugar, or the yield that is given when the impurity in the starch has been neutralized. Above this point we may continue to add acid until there are nearly two equivalents in excess, and still get the maximum yield. Then the acid begins to retard, but not nearly in the degree that it would if no salt were present. It may be that as soon as there is present a sufficient quantity of acid to give the maximum yield, a further addition will cause instant retardation, but it is so slight that it is impossible to detect it. The other acids behave in general in the same way; the retardation with formic commencing when $\frac{1}{5}$ of an equivalent is in excess, while propionic gives no sign of retarding action until four equivalents are in excess. It will be seen that the maximum yield is given within quite a large range (though this is probably due to lack of delicacy of the indicator), hence it is not strange that Duggan came to the erroneous conclusion that absolute neutrality was obtained by the addition of exact equivalents of acid in excess.[1]

[1] Since this paper has been put in type an article has appeared (Ztschr. phys. Chem. 12, 167) by Shields, who has been working with Arrhenius on this same problem. His method is wholly different from the one described in this paper, depending on the power of hydroxyl to saponify ethyl acetate. It will be interesting to see how future numerical results compare with the results obtained by him.

In conclusion I wish to make acknowledgment to Dr. Felix Lengfeld, at whose suggestion this work was undertaken, for the many suggestions, both practical and theoretical, that he has given me,

CHICAGO, *July*, 1893.

REVIEWS AND REPORTS.

RECENT PROGRESS IN PHYSICAL CHEMISTRY.—IV.

The Energy-Theory.

We learn from experience that heat, work, electricity, and the like are mutually convertible. They are therefore the same kind of thing, and this kind of thing has received the general name Energy.

The work of J. R. Meyer and of Helmholtz, a half-century ago, in straightforwardly stating the significance and bearing of the energy-conception, marked the dawning of a new era in the rational development of the physical sciences. A recognition of the great fact that energy is the actuality with which exact science has to deal is making it possible to pass from the more purely descriptive stages of scientific work to a systematic study of causal relations; to build upon this conception of energy a strict and coherent theory of phenomena.

In no department of science are the results already reached so full of promise as they are in chemistry. The mutual relations of heat, electricity, volume-energy, and the like in determining the character of chemical processes and the state of chemical systems are now clearly seen to be of fundamental importance. Chemists have waited long for this insight. It has been delayed by the obstinate and crude idea that all forms of energy are forms of mechanical energy, and that in consequence mechanical hypotheses are necessary for the explanation of natural phenomena. This belief arose, after the discovery of the mutual convertibility of heat and work, from the simple fact that the mechanical energies were the best known. For the old method is substituted a web of exact relations between the energy-phenomena coming in question. Physical theory and not mechanical hypothesis has become the guiding-star.

The energy-method, now coming to full fruition, has not been totally neglected in these intervening years, as is evinced by the

discoveries of Kirchhoff concerning solutions, by those of Helmholtz in electro-chemistry and chemical affinity, by the Intensity Law of Helm, and by the remarkable and yet too little understood theoretical work of our own countryman, Willard Gibbs.[1]

The different sciences would be wholly distinct were the several energy-forms which they treat not mutually convertible. This convertibility, and this alone, unites them into a general Science of Energetics. By using energy, space and time as the units common to them all,[2] there are obtained throughout measurable relations between them. The subjects of chemistry, electricity, heat and work are thus brought together, and the respective transformations of the energies involved furnish the subject-matter of the sciences of electro-chemistry, thermo-chemistry, electro-dynamics, thermodynamics and mechanics.

In a paper subsequent to the one cited, Ostwald directs especial attention[3] to the resolution of the analytical expressions of the various energy-forms into their factors, one of which has the character of an *intensity* of the energy-form in question, and the other that of a *capacity* for it. The intensity-factor determines whether its energy may or may not be at rest, having, by definition, the same value for two energy-quantities which do not influence each other. Examples of this resolution into factors are:

		Capacity.	Intensity.	Formula.
Mechanical energies.	Distance-energy	= distance	× force	$s.f$
	Surface-energy	= surface	× tension	$O.\gamma$
	Volume-energy	= volume	× pressure	$v.p$
	Motion-energy	= mass	× velocity square	$\frac{1}{2}m.V^2$
Other energies.	Electricity	= quantity	× potential	$\varepsilon.\pi$
	Heat	$= \frac{dQ}{dT}$ or $\left(\frac{Q}{T}\right)_\tau$	× temperature	$\frac{Q}{T}.T$
	Magnetism	= mag. quan.	× mag. potential	$e.H.$

The observed impossibility of creating energy from nothing, of creating the ultimate reality, is formulated as the First Law of Energetics: The energy of the universe is constant. A similar recognition of the impossibility of unlimited transformation of one energy-form into another without intensity-differences, as in obtaining work from a quantity of heat of uniform temperature or from electricity of uniform potential, constitutes the Second Law of Energetics: Unlimited conversion of an energy, without intensity-differences, is impossible.

The condition for the equilibrium of a single energy-form—that its intensity shall be uniform throughout—is, in its application, very familiar. The heat in a bar of iron, which is hot at one end,

[1] Trans. Conn. Acad. **3**; Thermodynamische Studien (translated by Ostwald), Leipzig, 1892.
[2] Ostwald: Ztschr. phys. Chem. **9**, 563 (1892).
[3] Ztschr. phys. Chem. **10**, 363 (1892).

will be transferred by conduction until the temperature-differences shall have become equalized; a mass of a gas must have uniform pressure throughout (the effect of gravitational energy supposed eliminated); electricity will not pass from one electrically charged body to another when both quantities of electricity have the same potential; two moving masses will not influence each other's motion if their velocities be the same (they must correspondingly have the same direction of motion, for the definition of a velocity includes a direction). The same rule applies to the other energy-forms.

But that feature of the energy-theory which is of the most especial interest at the present time, is its treatment of the equilibria between several energy-forms which oppose one another in the same system. Such an equilibrium is said to obtain when no transformation of one energy-form into another takes place. The equilibrium eventually reached may be disturbed by a change of the intensity-factor of any one of the energies involved, this causing an opposed change of the correlative energy-forms. At equilibrium, an infinitesimal change (virtual change) of one of the energies must be exactly balanced by the resulting virtual changes of the others.

The necessary and sufficient *condition of equilibrium*, then, for any material system whatsoever, is:

The algebraic sum of the energy-changes involved in a virtual displacement of the equilibrium must equal zero.[1]

If energy, capacity and intensity be represented by E, C and I, respectively, this condition is expressed analytically by

$$\Sigma\delta E = 0 \quad \text{or} \quad \Sigma C.dI = 0,$$

the summation being taken over all the correlated energies of the system. It is known as the Principle of Virtual Energies, and it represents the theory of all equilibria whatever, whether they be those of statics, of thermodynamics, of chemistry, or of any other branch of general energetics. This is the most important element of Ostwald's work in the energy-theory.

Systematic application of this principle of virtual energies has shown strikingly the analogy in character between various important and apparently heterogeneous relations.

The amount of work gained in the isothermal expansion of a dissolved substance, or of a gas, from a given initial pressure P to a lesser one p is

$$\int dW = -\int_p^P v\,dp$$

$$= -RT\int_p^P \frac{dP}{P},$$

$$W = RT\log\frac{P}{p},$$

[1] Ostwald, l. c. 1892.

the integration being effected with the aid of the equation of condition of dilute matter, $pv = RT$. The resulting equation, giving the work-value of a concentration-change in a dilute solution (van't Hoff, 1887), or in a voltaic cell (Nernst, 1889), is a fundamental one in the theory of solutions and in electro-chemistry.

Other differential equations of the same form $\Sigma C dI = 0$, but not integrable in this way, express the mutual dependence of (1) electricity, (2) surface-energy, (3) heat, (4) volume-energy. Arranged in order, they are—

For the equilibrium between electricity and surface-energy:

$$O d\gamma = -\varepsilon d\pi,$$
$$\frac{d\gamma}{d\pi} = \frac{-\varepsilon}{O},$$

the relation between surface-tension and electromotive force.

That between surface-energy and heat:

$$\frac{q}{T} . dT = O . d\gamma,$$
$$\frac{d\gamma}{dT} = \frac{q}{T . O},$$

an expression for the temperature-coefficient of surface-tension.

That between electricity and heat:

$$\varepsilon d\pi = \frac{q}{T} . dT,$$
$$\frac{d\pi}{dT} = \frac{q}{T . \varepsilon},$$

the famous equation of Gibbs and Helmholtz, introducing the element of temperature into the theory of electro-chemistry.

That between heat and volume-energy [$(v' - v)$ = increase of molecular volume caused by the change considered],

$$\frac{q}{T} dt = (v' - v)\, dp,$$
$$\frac{dp}{dt} = \frac{q}{T(v' - v)},$$

a relation comprehending the extremely extended theory of such changes of state as are involved in the processes of vaporization, sublimation, dissolving, melting and the transformation of allotropic forms. It is familiarly known as the Clausius vaporization-formula.

All these special cases of the equation are of the form

$$c' . dI' = c . dI$$

or

$$\frac{dI'}{dI} = \frac{c}{c'},$$

and they express the details of what is known as the Theory of the "Complete" Chemical Equilibria.

In a paper read at the World's Congress at Chicago, the writer has pointed out the bearing of the energy-theory in expressing the influence of extraneous energy-forms upon the purely chemical volume-energy equilibria of reversible reactions. When a system of reacting substances is in equilibrium, the total virtual change Σvdp of the volume-energy of the reaction-products is balanced by that ΣVdP of the original substances. p and v represent throughout the partial pressures and reacting volumes of the substances in question, and when the system is left to itself, the fundamental equation (3) assumes the form

$$\Sigma vdp - \Sigma VdP = 0.$$

With the aid of the general "equation of condition" of dilute matter, $pv = nRT$, whence $p = nRTv^{-1}$ and $dp = -nRT\frac{dv}{v^2}$, we can eliminate the pressure-factor, obtaining

$$-RT(n\Sigma d \log v - \Sigma d \log V) = 0,$$

whence, at constant temperature, replacing the molecular volume by its reciprocal, the molecular concentration,

$$\Sigma \partial \log c^n = \Sigma \partial \log C^N.$$

The integral of this equation furnishes the concentration-relations for a chemical equilibrium at constant temperature,

$$\Sigma \log c^n + \log k' = \Sigma \log C^N + \log k,$$

i. e.

$$\frac{c_1^{n_1}.c_2^{n_2}\ldots}{C_1^{N_1}.C_2^{N_2}\ldots} = \frac{k}{k'} = K,$$

or

$$c_1^{n_1}.c_2^{n_2}\ldots = K.C_1^{N_1}.C_2^{N_2}\ldots,$$

which states the effect of each reacting substance to be proportional to its concentration; K is the "equilibrium-constant." This is the famous Law of Mass-Action, expressing the conditions of chemical equilibrium at constant temperature.

Further, if pressure be applied to a system of reacting substances, work is done upon the system and a deformation of its chemical equilibrium results. The principle of virtual energies represents this equilibrium between volume-energy and work in the form

$$-\Delta v.dp - (\Sigma vdp - \Sigma VdP) = 0,$$

where $-\Delta v$ is the volume-decrease accompanying the reaction in question, and is a function of the molecular volumes of the substances. The bracketed expression has been already found to be $RT\partial \log K$, K being at a given temperature the constant *characterizing* the equilibrium. So we have

$$\frac{\partial \log K}{\partial p} = \frac{-\Delta v}{RT},$$

expressing the effect of pressure upon a chemical equilibrium.

One more case remains under this head, that concerned with the influence of temperature upon a movable equilibrium. On adding the heat-quantity Q to a chemical system, the resulting balance between it and the volume-energy change of the displaced chemical equilibrium is

$$\frac{Q}{T} \cdot dT - (\Sigma v dp - \Sigma V dP) = 0,$$

$$\frac{Q}{T} \cdot dT - RT\partial \log K = 0,$$

$$\frac{\partial \log K}{\partial T} = \frac{Q}{RT^2}.$$

This equation connects the influence of temperature with the heat of reaction. Its applications to chemical phenomena have been extended and are brilliant in the extreme.

Since the idea of chemical affinity is not always an entirely clear one, it may be in place to add a few words about it from the energy point of view. Chemical action usually effects changes in the state of aggregation or in the density of the substances concerned, and so produces work (or other energy-forms—*e. g.*, electricity—entirely convertible into work), as well as heat. A distinction must therefore be made between that part of the available energy capable of direct conversion into work and that part producible only as heat. The first is appropriately termed the *free energy*, the second the *bound energy* of the system.

A spontaneously-occurring natural process is one taking up no energy other than heat from the surrounding medium. Every such process may be made to yield a definite maximum amount of work. For, if its available work were negative it would have to take place without absorption of energy, and on being reversed by the addition of heat would transform this heat into work. The operation might be indefinitely repeated, continually converting heat of constant temperature into work, a result in conflict with the Second Law of Energy.

Since every spontaneous process must yield work, a system incapable of doing so (one whose *free energy* has minimum value) is incapable of spontaneous change—is in stable equilibrium. So this condition of equilibrium, deduced from the Second Law of Energy, is: *The decrease of free energy must be a maximum.*[1]

Processes originating spontaneously and proceeding at constant temperature can take place only in such direction as to cause a diminution of free energy, a production of energy-forms convert-

[1] Helmholtz, 1882.

ible without limit ("work"). It is therefore the decrease of free energy, and not the heat developed, which determines the direction in which chemical affinities can become active, *and which is the measure of the work-value of the chemical forces.*

Of all possible chemical changes in a material system the one involving the greatest decrease of its free energy (the maximum available work) will occur. Neither the reaction involving maximum production of heat, nor that of maximum thermal tonality (sum of heat and work produced), will necessarily take place; there are in fact many spontaneously-occurring chemical processes which absorb heat. The decrease of free energy in any given reaction is found by determining the work to be gained when the transformation is made reversible and isothermal.

An especially important feature of the energy-theory is its entire disregard of assumptions and hypotheses. In dealing directly with known facts, the results which it reaches are of necessity actual relations between measurable quantities. Among them are the remarkable relations which form the framework of thermodynamics, of electro-chemistry, of chemical equilibrium, of the solution-theory. The mutual dependence of vapor-pressure and heat, of vaporization, of electromotive force and heat of reaction, of reaction-velocity and temperature, of the freezing-point of a solution and the heat of fusion of its solvent, are among the most brilliant results of exact science. TREVOR.

A DICTIONARY OF APPLIED CHEMISTRY. By T. E. THORPE, B. Sc. (Vict.), Ph. D., F. R. S., assisted by eminent contributors. In three volumes. Vol. 3. London and New York: Longmans, Green & Co., 1893. 1058 pages. 8vo.

Vols. 1 and 2 of this very valuable work have formed the subject of notices at the time of their appearance. Both Professor Thorpe and his brother chemists are to be congratulated upon the completion of their labor. It is safe to assert that there is no better book on applied chemistry in any language, and it is essential to every chemical library. There appears to be no better way of conveying an idea of the character of the book than by giving a partial list of the important articles and their authors. The subject of Fixed Oils and Fats has been treated by A. H. Allen; Paper, by E. J. Bevan; Water, by Percy F. Frankland; Spectrum Analysis, by W. N. Hartley; Starch and Saccharimetry, by John Herron; Stearin and Commercial Stearic Acid, by G. T. Holloway; Persian Berries, Quercitron Bark, Safflower, Turmeric, Weld, and Woad, by J. J. Hummell; Phthalic Acid, Quinone and Quinones, Salicylic Aldehyde, Thiophen, Toluene, by F. R. Japp; Salts of Potassium, Sodium Sulphate, Sodium

Carbonates and Caustic Soda, by G. Lunge; Sugar, by J. A. R. and B. E. R. Newlands; Pyrotechny, by G. S. Newth; Solution, by W. W. J. Nicol; Ultramarine, by G. W. Rawlins; Phosphorus, by J. B. Readman; American Petroleum, by S. P. Sadtler; Photography, by J. M. Thomson; Essential Oils, Resin, and Terpenes, by W. A. Tilden; Triphenylmethane Coloring Matters, by Otto N. Witt; Soap, Sulphur, Sulphuric Acid, by C. R. Alder Wright; Phenol, Picric Acid, Quinoline, by W. P. Wynne; Thermometers, by Sydney Young.

The names of the authors furnish strong evidence as to the character of the book. No one person could intelligently review it. Among the articles that appeal most strongly to the general chemist are, of course, those on Water, Triphenylamine Coloring Matters, Photography, and Sodium Compounds. These are admirably written, and are good examples of what dictionary articles should be.

It is to be hoped that not many errors are contained in the work like that pertaining to the discovery of Saccharin—a small matter in itself, to be sure, but worth noting, and of some little interest, especially to the writer of this notice. I. R.

HAND- UND HILFSBUCH ZUR AUSFUEHRUNG PHYSIKO-CHEMISCHER MESSUNGEN. W. OSTWALD. Leipzig: Engelmann, 1893. (8 Marks.)

In this handy little volume of three hundred pages, Ostwald has condensed the results of his extended and very exceptional experience in the practical details of the conduction of research in physical chemistry. The chapters treating glass-blowing, weighing, and the determination of solubilities and of molecular weights, contain many valuable suggestions about these ordinary manipulations of the laboratory. Those on the determination of temperatures, pressures, densities, surface-tensions, heat-quantities and critical data, together with those on optical and electrical measurements, are necessarily of more special interest. The descriptions and explanations are admirably clear, the book is practically arranged and well printed, and it is accompanied by various separately printed tables which materially enhance its practical value. J. E. T.

NOTES

EDITOR AMERICAN CHEMICAL JOURNAL:

In the Journal for May 1 notice, on page 375—"Studies on the Properties of Carbon and the Preparation of Diamond"—the statement that the meteorite described by Henri Moissan was the first in which diamonds were found. This is an error. There was a meteorite which fell September 22, 1886, near Nowo Urei, Government of Pensa, Russia, and was found by M. Zerofereff and P. Latschinoff to contain one per cent. of ordinary diamond.[1]

Another instance of great interest was the discovery made by Prof. A. E. Foote, of this city, of meteoric iron containing diamonds, in the Cañon Diablo, Arizona.[2] A prospector in Arizona reported a vein of metallic iron near Cañon Diablo. This so-called vein was examined by Prof. Foote, who found, scattered over an area of over one-third of a mile, 131 small meteorites ranging in weight from 1.79 grams to 3 kilograms. Several large specimens were also found. The largest mass weighed 201 pounds, and was flattened and rectangular in shape, showing three large pits which pass through the iron. Another mass weighed 154 pounds and was also pitted. Another mass, weighing 40 pounds, was broken with a trip-hammer, and it was in this specimen that diamonds were found. It was sent to Prof. G. H. Kœnig, of the University of Pennsylvania, for analysis and examination. In cutting the meteorite it was found to be unusually hard; the section took a day and a half, and a number of chisels were destroyed. In polishing the surface to bring out the Widmannstättian figures, the emery wheel was broken; it had passed through a cavity containing diamonds which cut it through. The diamonds were both black and white. The white specimen was half a millimeter in diameter. Carbide of iron was also found in the same cavity. The meteorite contained sulphur, phosphorus, cobalt, silicon, iron and nickel; the last-mentioned amounted to but 3 per cent. The specimen described by Henri Moissan was one of those found in Cañon Diablo and was presented to the French Academy.

CENTRAL HIGH SCHOOL, PHILADELPHIA, *Nov.* 2, 1893. OSCAR C. S. CARTER.

THE American Academy of Arts and Sciences, at a meeting held in Boston, November 8, voted to grant—from the C. M. Warren Fund for Encouraging Chemical Research—the sum of $300 to Professor C. F. Mabery of Cleveland, Ohio, in aid of his Investigations on the American Sulphur Petroleums.

[1] Am. J. Sci. [3] **36**, 74. [2] *Ibid.* [3] **42**, 413.